

The role of protons in cyclohexene oxidation with H₂O₂ catalysed by Ti(IV)-monosubstituted Keggin polyoxometalate

Oxana A. Kholdeeva*, Tatiana A. Trubitsina, Maria N. Timofeeva, Gennadii M. Maksimov, Raisa I. Maksimovskaya, Vladimir A. Rogov

Boreshkov Institute of Catalysis, Pr. Ac. Lavrentieva 5, Novosibirsk 630090, Russia

Received 16 September 2004; received in revised form 29 October 2004; accepted 26 January 2005

Abstract

The effect of the number of protons in the Ti(IV)-monosubstituted Keggin polyoxometalate Na_{5-n}H_nPTiW₁₁O₄₀ ($n = 1-5$; Ti-POM) on its catalytic behaviour in cyclohexene (CyH) oxidation with aqueous H₂O₂ in MeCN is reported. It has been found that Ti-POMs with $n = 2-5$ catalyse efficiently CyH oxidation to yield *trans*-cyclohexane-1,2-diol as the main reaction product, while Ti-POM containing only one proton shows lower activity in CyH oxidation and produces allylic oxidation products, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, along with comparable amounts of the corresponding epoxide and diol. The obtained results strongly support homolytic oxidation mechanism for CyH oxidation in the presence of the monoprotonated Ti-POM and heterolytic oxygen-transfer mechanism in the presence of Ti-POMs having two and more protons. The ³¹P and ¹⁸³W NMR studies revealed that Ti-POMs are stable towards at least 100-fold excess of H₂O₂ and the high catalytic activity of Ti-POMs with $n = 2-5$ is not due to the formation of lower nuclearity species. The addition of one equivalent of H⁺ to the monoprotonated peroxo complex [Bu₄N]₄[HPTi(O₂)W₁₁O₃₉] (**I**, ³¹P NMR in MeCN: -12.40 ppm) results in the formation of the diprotonated titanium peroxo species [H₂PTi(O₂)W₁₁O₃₉]³⁻ (**II**, ³¹P NMR in MeCN: -12.14 ppm). This peroxo species can also be obtained by adding an excess of H₂O₂ to Na_{5-n}H_nPTiW₁₁O₄₀ ($n = 2-5$) in MeCN. The presence of the second proton in the peroxo species is a crucial factor determining the capability of **II** to oxidise alkenes via heterolytic oxygen transfer mechanism. Both ³¹P NMR and GC-MS studies corroborated that **II** reacts with CyH producing *trans*-cyclohexane-1,2-diol as the main reaction product, whereas **I** is not reactive towards CyH under stoichiometric conditions.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Ti-substituted polyoxometalate; Cyclohexene; H₂O₂; Peroxotitanium species; Oxidation mechanism

1. Introduction

The selective catalytic oxidation of organic compounds with a “green” oxidant, aqueous H₂O₂, is highly desirable [1–10]. In particular, cyclohexene (CyH) oxidation to cyclohexene oxide followed by epoxide ring opening and subsequent oxidation of *trans*-cyclohexane-1,2-diol rates as a possible route to adipic acid [11–16]. d-Electron-transition-metal-oxygen-anion clusters (polyoxometalates or POMs for short) have attracted much attention as oxidation catalysts due to their hydrolytic and thermal stability, solubility

in various media, tunable acid and redox properties, etc. [17–25]. Yet, POMs have metal-oxide like structure and thus can be viewed as tractable homogeneous models for studying oxidation mechanisms [26–33].

Both homogeneous and heterogeneous H₂O₂-based alkene oxidation catalysed by POMs has been reported [18–25,34–48]. Several ³¹P NMR studies implicated that most of POMs are not stable under turnover conditions of H₂O₂-based oxidations and, in fact, act as precursors of a true catalyst, e.g. Venturello complex {PO₄[M(O)(O₂)₂]₄}³⁻ (M = Mo, W), and/or other active low nuclearity species [23,49–52]. Few POMs really stable towards H₂O₂ have been reported [23,39]. Among them is the titanium-monosubstituted dimeric heteropolytungstate

* Corresponding author. Tel.: +7 3832 309573; fax: +7 3832 308056.

E-mail address: khold@catalysis.nsk.su (O.A. Kholdeeva).

[Bu₄N]₇[(PTiW₁₁O₃₉)₂OH] (**1**), the Keggin structural unit of which, [PTiW₁₁O₄₀]⁵⁻ (**2**, Ti-POM), is resistant towards oxidative degradation in MeCN in the presence of a 1000-fold excess of H₂O₂ [30]. Recently, we have isolated and comprehensively characterised the monoprotonated titanium peroxo complex [Bu₄N]₄[HPTi(O₂)W₁₁O₃₉] (**I**), formed upon interaction of **1** with aqueous H₂O₂ in MeCN, and demonstrated its reactivity towards 2,3,6-trimethylphenol under both stoichiometric and catalytic conditions [33].

Here, we would like to show our progress in studying oxidation mechanisms using Ti-POMs as soluble model compounds and report a comparative study of cyclohexene oxidation by H₂O₂ in the presence of **1**, heteropolyacid H₅PTiW₁₁O₄₀ (H₅-**2**), and acid sodium salts Na_{5-n}H_nPTiW₁₁O₄₀ (Na_{5-n}H_n-**2**, *n* = 1–4). This work first demonstrates how the composition of the cationic part of Ti-POM, specifically the number of protons, can control the oxidation mechanism and, therefore, the oxidation products.

2. Experimental

2.1. Materials and catalysts

Acetonitrile (Fluka) was dried and stored over activated 4 Å molecular sieves. H₂O₂ (30 wt% in water) was titrated iodometrically prior to use. H₂O₂ (10%) was prepared by dilution of 30% H₂O₂ with water. Cyclohexene, cyclohexene oxide, *trans*-cyclohexane-1,2-diol, 2-cyclohexene-1-ol and 2-cyclohexene-1-one were purchased from Fluka. All the other reactants were the best available reagent grade and were used without further purification. Heteropolyacid H₅PTiW₁₁O₄₀·8H₂O (H₅-**2**) was synthesised by the electrodialysis method as described previously [53–55]. ³¹P NMR (–δ): 13.67 and 12.16 ppm in H₂O and MeCN, respectively. Acid sodium salts Na_{5-n}H_nPTiW₁₁O₄₀ (Na_{5-n}H_n-**2**, *n* = 1–4) were prepared by adding the corresponding stoichiometric amounts of NaHCO₃ to an aqueous solution of H₅-**2** followed by evaporation of water. Elemental analysis (Na, found/calculated): 3.05/3.13, 2.46/2.37, 1.60/1.60, and 0.80/0.80 for *n* = 1, 2, 3, and 4, respectively. ³¹P NMR in MeCN (–δ): 13.10, 12.23, 12.17, and 12.16 ppm for *n* = 1, 2, 3, and 4, respectively. Synthesis of TBA₇[(PTiW₁₁O₃₉)₂OH] (**1**) was performed as described earlier (³¹P NMR in dry MeCN: –12.76 ppm) [30]. Venturello complex [CH₃N(C₈H₁₇)₃]₃{PO₄[W(O)(O₂)₂]₄} (**3**) was synthesised according to [34]. The monoprotonated titanium peroxo complex, [Bu₄N]₄[HPTi(O₂)W₁₁O₃₉] (**I**), was prepared as described in [33]. The purity of all the synthesised POMs was checked by elemental analysis, IR and ³¹P NMR. The diprotonated titanium peroxo species was generated in situ by adding one equivalent of H⁺ (in the form of triflic acid) to **I**. ³¹P NMR in MeCN (δ): –12.14 ppm.

2.2. Oxidation of cyclohexene (CyH)

Catalytic oxidations of CyH with H₂O₂ in the presence of Ti-POMs were carried out in temperature-controlled glass vessels at 70 °C, [POM] = 0.01, [CyH] = 0.2 and [H₂O₂] = 0.4 M in MeCN (3 ml) for 5 h. Biphenyl was added as an internal standard for GC. Aliquots were taken during the reaction course and analysed by GC and GC–MS. Stoichiometric oxidation of CyH was carried out at [I] = 0.02 M, [H⁺] = 0.02 M, and [CyH] = 0.1 M. Acid was added to a preliminarily cooled MeCN solution, containing **I** and CyH, and then the reaction was followed by both ³¹P NMR and GC–MS.

2.3. Instrumentation and methods

CyH conversion was determined by GC using a gas chromatograph ‘Tsvet-500’ equipped with a flame ionisation detector and a 30 m × 0.25 mm Supelco capillary column filled with MDN-5S. The oxidation products were identified by means of GC–MS and GC using authentic samples. For GC–MS analyses, a Saturn 2000 gas chromatograph equipped with a CP-3800 mass spectrometer was used. The ¹⁸³W NMR spectra were run on an MSL-400 Brüker NMR spectrometer at operating frequency of 16.67 MHz, with 2.5 kHz sweep width, 50 μs pulse width and 5 s pulse delay. The corresponding parameters for ³¹P NMR were 161.98 MHz, 5 kHz, 10 μs, 30 s. Chemical shifts, δ, were referenced to 85% H₃PO₄ and 1 M aqueous Na₂WO₄; the error in measuring δ was in the range of ±0.05 and 0.1 ppm for ³¹P and ¹⁸³W NMR spectra, respectively. The IR spectra of POMs were recorded for 0.5–1.0 wt.% samples in KBr on a Specord-75 IR.

3. Results and discussion

In our previous work, we revealed that dimer **1** dissociates to the monomer [Bu₄N]₄[PTi(OH)W₁₁O₃₉] (TBA₄H-**2**) when H₂O is added to a MeCN of **1** [30,31,55]. The results on CyH oxidation with aqueous hydrogen peroxide catalysed by **1** (in fact, TBA₄H-**2**), H₅-**2** and acid sodium salts Na_{5-n}H_n-**2** (*n* = 1–4) are given in Table 1. In the presence of TBA₄H-**2**, CyH conversion was rather low (run 1), and allylic oxidation products, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, were found along with comparable amounts of the corresponding epoxide and diol. In contrast, the catalytic activity of both H₅-**2** and Na_{5-n}H_n-**2** (*n* = 2–4) was significantly higher and similar to that of the Venturello complex (compare runs 2–6 and 8). However, while **3** in accordance with literature [34], gave a high yield of epoxide, *trans*-cyclohexane-1,2-diol predominated among the oxidation products obtained in the presence of H₅-**2** and Na_{5-n}H_n-**2** (*n* = 2–4). This is not surprising keeping in mind high Brønsted acidity of H₅-**2** [56], which should promote epoxide ring opening. Earlier, it was reported that

Table 1
Cyclohexene oxidation with 30% H₂O₂ catalysed by POMs^a

Run	POM	CyH conversion (%)	Product yield ^b (%)			
			Epoxide	Diol	En-ol	En-one
1	TBA ₄ H-2	26	4	9	2	11
2	H ₅ -2	80	4	56	4	2
3	H ₅ -2 ^c	79	2	69	2	Trace
4	NaH ₄ -2	84	6	63	2	4
5	Na ₂ H ₃ -2	84	8	56	1	6
6	Na ₃ H ₂ -2	75	8	54	2	5
7	Na ₄ H-2	70	14	30	5	20
8	3	96	81	10	Trace	4
9	–	4	2	Trace	1	0.3
10	H ₃ PW ₁₂ O ₄₀ ^c	41	25	14	1	Trace
11	H ₄ SiW ₁₂ O ₄₀ ^c	16	10	Trace	4	Trace

^a Reaction conditions: CyH 0.2 M, H₂O₂ (30%) 0.4 M, POM 0.01 M, MeCN 3 ml, 70 °C, 5 h.

^b GC yield based on initial CyH.

^c 10% H₂O₂ was used instead of 30% H₂O₂.

the Venturello complex also produces *vic*-diols with high yields under two-phase conditions when pH of aqueous phase is in the range of 1.5–2.3 [36]. With Na₄H-2 as catalyst (run 7), CyH conversion was higher than that with TBA₄H-2 (run 1); however, the yield of the allylic oxidation products increased compared to Na_{5–n}H_n-2 with $n = 2–4$. Importantly, without any POM used, cyclohexene conversion was only 4% (Table 1, run 9). In the absence of H₂O₂, the conversion was also negligible. It has been reported that acids are capable of catalysing alkene epoxidation with H₂O₂, most likely via formation of active H₃O₂⁺ species [57,58]. In this case, a rate-reducing effect of water is to be expected [57,58]. Meanwhile, we have found that CyH conversion in the presence of H₅-2 does not decrease with increasing concentration of water (compare runs 2 and 3). Moreover, the selectivity towards diol enhances when 10% H₂O₂ is used instead of 30% H₂O₂. Heteropolyacid H₄SiW₁₂O₄₀, which is rather stable to oxidative degradation [23,49–51] and has stronger Brønsted acidity in MeCN than H₅-2 does [56], is less active (run 11) in CyH oxidation with H₂O₂ compared to H₅-2. On the contrary, H₃PW₁₂O₄₀, which is known to degrade rapidly yielding lower nuclearity species including **3** [23,49–51], gave a noticeable yield of epoxide and diol (run 10). These data are consistent with the data published in the literature [38]. Both the lack of the rate-reducing effect of water and low activity of H₄SiW₁₂O₄₀ indicate that CyH oxidation with H₂O₂ in the presence of **2** is not a simple acid-catalysed reaction. Thus, the presence of both titanium and acid centres is crucial for high catalytic activity of Ti-POMs just as it was established earlier for titanium-silicate catalysts [59–62]. Furthermore, at least two protons per Ti-POM are necessary for efficient CyH conversion to the corresponding diol (compare runs 2–6 with runs 1 and 7).

The present study clearly shows that the number of protons in Ti-POM has a high impact on the distribution of CyH oxidation products, unambiguously indicating that different oxidation mechanisms operate depending on the

Table 2
³¹P NMR data for H₅PTiW₁₁O₄₀ and its acid sodium salts

POM ^a	³¹ P NMR in MeCN, – δ (ppm)	
	Before addition of H ₂ O ₂	After addition of H ₂ O ₂ ^b
H ₅ -2	12.16	12.09; 12.55
NaH ₄ -2	12.16 (12.38) ^c	12.08; 12.54
Na ₂ H ₃ -2	12.17	12.09; 12.56
Na ₃ H ₂ -2	12.23	12.16; 12.71
Na ₄ H-2	13.10	12.25; 13.08

^a [POM] = 0.01 M.

^b [H₂O₂] = 0.15 M.

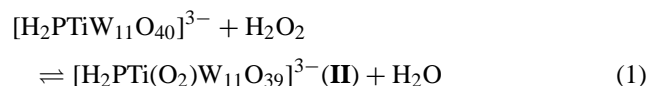
^c After addition of 6 μ L H₂O to 4 mL of MeCN.

H⁺/Na⁺ ratio in Ti-POM. Note that CyH is widely used as a test substrate, which allows one to distinguish between one-electron and two-electron oxidation mechanisms. The formation of allylic oxidation products along with epoxide and diol is associated with a homolytic oxidation mechanism, while selective formation of epoxide (diol) evidences in favour of a heterolytic oxidation mechanism via oxygen atom transfer [22,23,63,64]. The obtained results (Table 1) strongly support the homolytic oxidation mechanism for CyH oxidation in the presence of the monoprotonated Ti-POMs, TBA₄H-2 and Na₄H-2. Recently, we have found that oxidation of thioethers and alkylphenols with H₂O₂ in the presence of **1** also proceeds via homolytic electron-transfer mechanisms [31–33]. At the same time, the oxygen-transfer mechanism most likely predominates in the presence of Ti-POMs having two and more protons, such as Na_{5–n}H_n-2 ($n = 2–5$).

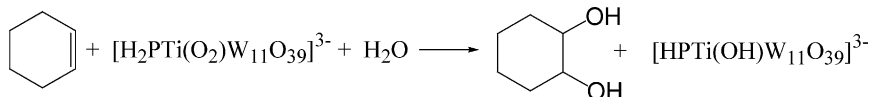
To understand the nature of the catalytic activity of **2**, we examined both H₅-2 and Na_{5–n}H_n-2 ($n = 1–4$) using ³¹P and ¹⁸³W NMR in MeCN in the presence of a 15–100-fold excess of H₂O₂. First, upon addition of H₂O₂ to Ti-POMs ([H₂O₂]/[**2**] = 100) and storing the solution at 70 °C for at least 5 h, no products derived from degradation of the Keggin structural unit were detected by ³¹P NMR in the range of +7 to –22 ppm. Second, simultaneously with fast appearance of an orange colour, which is characteristic of titanium peroxy complexes [30,32,65,66], the ³¹P NMR signal of the initial Ti-POM moved upfield and its intensity decreased, while a new signal in the range of $\delta = 12.08$ to 12.25 ppm appeared (Table 2).

It has been previously established that ³¹P chemical shift of protonated POM species is greatly affected by the presence of H₂O in organic solvent because water competes for protons with POM [30, and references therein]. The upfield shift of the initial ³¹P NMR peak of H₅-2 after addition of H₂O₂ is most likely due to water present in aqueous H₂O₂ (chemical shifts of H₅-2 are –12.16 and –13.67 in dry MeCN and H₂O, respectively). Indeed, the addition of 6 μ L of H₂O to a MeCN solution of NaH₄-2 resulted in shifting of the ³¹P NMR signal to –12.38 ppm. We assigned the new signal appearing at –12.09 ppm after the addition of H₂O₂ to Na_{5–n}H_n-2 ($n = 3–5$) to peroxy species **II**, the formation of

which can be tentatively described by Eq. (1).



Indeed, the addition of one equivalent of H^+ to **I** ($\delta -12.40$ in MeCN) resulted in shifting of the ^{31}P resonance to -12.14 ppm, which coincides within the experimental error (0.05 ppm) with the signal of **II** obtained via reaction (1). This confirms the assignment of the ^{31}P NMR peaks made above (Table 2) and agrees with the previous findings that ^{31}P NMR signals move downfield upon protonation of POMs. Thus, we observed downfield shift of the ^{31}P NMR signal upon protonation of the peroxo complex $[\text{Bu}_4\text{N}]_5[\text{PTi}(\text{O}_2)\text{W}_{11}\text{O}_{39}]$ (**III**) [65,66] in dry MeCN [30] and upfield shift upon deprotonation of **I** [33]. Changes in ^{31}P NMR spectra were observed also for Bu_4N -salts of $[\text{PCoW}_{11}\text{O}_{39}]^{5-}$ upon protonation and deprotonation of the heteropoly anion [67]. Importantly, subsequent addition of the second, third and fourth equivalents of protons to **I** did not cause further shifting of the ^{31}P NMR signal. That means that two is the maximal number of protons, which are bound to the Keggin Ti-POM peroxo anion in dry MeCN. This is in agreement with the ^{31}P NMR data given in Table 2. Indeed, ^{31}P resonances of both initial $\text{Na}_{5-n}\text{H}_n\text{-2}$ and their peroxo derivatives have the same chemical shifts when $n = 3-5$, indicating that first three protons completely dissociate in MeCN.



The ^{183}W NMR spectrum of **II** (Fig. 1) run after addition of a 15-fold molar excess of H_2O_2 to $\text{NaH}_4\text{-2}$ (0.1 M in MeCN) consists of six lines ($-\delta$ 95.9, 110.2, 111.8, 114.0, 117.1 and 137.8) with an intensity ratio of 2:2:2:2:1:2, indicating the C_s symmetry of the anion and thus confirming the retention of the Keggin structural unit. The disposition of the peaks in the ^{183}W NMR spectrum of **II** differs from that of monoprotonated peroxo complex **I** [33].

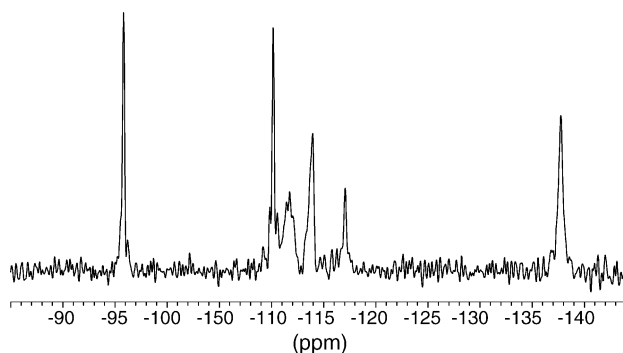


Fig. 1. ^{183}W NMR spectrum of **II** generated in situ via addition of a 15-fold molar excess of H_2O_2 to $\text{NaH}_4\text{-2}$ (0.1 M in MeCN).

The number of protons drastically affects the reactivity of the Ti-POM peroxo complexes. It has been well established that peroxo complex **III** is inert towards oxidation of organic substrates under stoichiometric conditions [30,33,41]. In turn, monoprotonated peroxo complex **I** is capable of oxidising thioethers [30–32] and alkylphenols [33] via one-electron mechanism but is not reactive towards alkenes, specifically, cyclohexene. Our attempts to isolate **II** failed because of high reactivity of this species. To study reactivity of **II** towards CyH, we generated it in situ by adding one equivalent of H^+ to a preliminarily cooled MeCN solution, containing **I** and CyH, and followed the reaction by both ^{31}P NMR (Fig. 2) and GC–MS. Since **II** is highly reactive, CyH should be added to **I** before the addition of acid, otherwise the reaction is too fast to follow it by ^{31}P NMR. The addition of CyH to **I** does not influence the position of the ^{31}P NMR signal of **I** ($\delta -12.4$; weak signals at -13.4 and -14.6 ppm belong to admixtures of $\text{TBA}_4\text{H-2}$ and $\text{TBA}_3\text{PW}_{12}\text{O}_{40}$, respectively). Upon addition of acid the orange solution of the peroxo species becomes colourless within a few minutes. In the ^{31}P NMR spectrum, the signal of **II** ($\delta -12.14$) first arises, then its intensity rapidly decreases (simultaneously with the decolouration of the solution), and a signal at -12.56 ppm gradually appears (Fig. 2A(b–e)). The latter signal can be assigned to protonated **2**. The formation of a derivative of **2** with the reaction product, *trans*-cyclohexane-1,2-diol, may also occur. The diol was detected by GC–MS thus indicating that the decay of the signal of **II** is really due to the reaction between **II** and CyH.

Finally, we would like to discuss the question about localisation of the activating protons in **II**. In principle, there are five positions in the molecule of the Ti-POM peroxo complex, where localisation of protons might be assumed. These are one peroxo oxygen atom attached to titanium and four Ti–O–W bridging oxygen atoms, where an excessive negative charge is to be expected [33,68,69]. The resonance Raman and DFT studies made on **I** and **III** implicated that at least one of the Ti–O–W bridges is protonated before the O–O group [33]. The second proton can be localised either at another Ti–O–W bridge (Scheme 1, structure **IIa**) or at the peroxo oxygen (structure **IIb**). We believe that the drastic change in the reactivity of the Ti-POM peroxo complex toward CyH and the alteration of the reaction mechanism, both occurring after appearance of the second proton in the Ti-POM molecule, may indicate that the second proton, in contrast to the first one, is bound to the peroxo oxygen (Scheme 1, structure **IIb**) thus activating the peroxo group to oxygen atom transfer. In solution, especially in the presence of some water, delocalisation of protons (H_3O^+) between Ti–O–W bridges and O–O group may occur. Future experimental and theoretical studies could shed light on this matter.

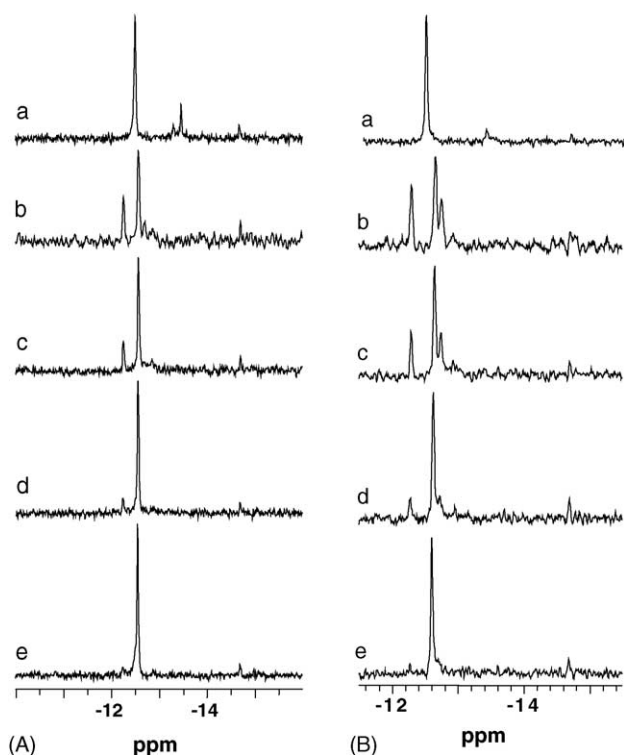
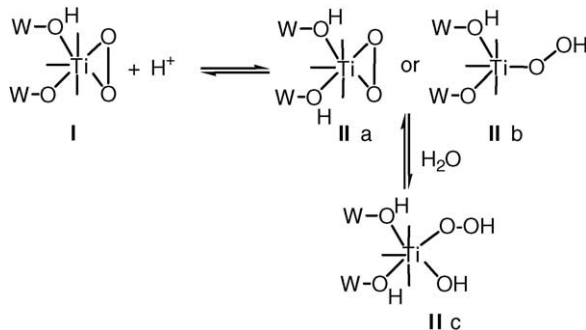


Fig. 2. (A) ^{31}P NMR spectra of (a) $[\text{Bu}_4\text{N}]_4[\text{HPTi}(\text{O}_2)\text{W}_{11}\text{O}_{39}]$ (**I**, 0.02 M) + CyH 0.1 M; (b) immediately after addition of one equivalent of H^+ to (a); (c) after 1 min; (d) after 3 min; (e) after 8 min. (B) The same as (A) but with 28 μl (0.4 M) H_2O added to (a).



Scheme 1.

Interestingly, when a small amount of water (0.4 M) was added to MeCN solution of **I** and CyH, and then one equivalent of acid was introduced, a new peak at $\delta -12.65$ arose and disappeared simultaneously with the peak at $\delta -12.14$ (Fig. 2B). We assume that the signal at $\delta -12.65$ might belong to another form of peroxo species **II**, probably to its hydrated form **IIc** (Scheme 1), which is also active towards CyH. Note that structures similar to **IIa–c** were suggested for active catalytic sites of titanium-silicates [59–62].

4. Conclusions

Four main conclusions can be drawn from the present work. First, heteropolyacid $\text{H}_5\text{PTiW}_{11}\text{O}_{40}$ and its acid

sodium salts $\text{Na}_{5-n}\text{H}_n\text{PTiW}_{11}\text{O}_{40}$ with $n=2-4$ catalyse effectively oxidation of cyclohexene with H_2O_2 producing *trans*-cyclohexane-1,2-diol as the main oxidation product, while Ti-POMs with lower proton content show lower activity in this reaction and yield allylic oxidation products along with epoxide and diol. Second, the revealed effect of the composition of Ti-POM cationic part on the product distribution suggests that the oxidation mechanism changes from a homolytic one to heterolytic oxygen transfer when amount of protons in Ti-POM increases from 1 to 2. Third, apparent contradictions occurring in literature on the catalytic activity of Ti-POMs in alkene oxidation may be due to lack of reliable control of the composition of the polyoxometalate cationic part (the number of protons). Fourth, the catalytic activity of $\text{Na}_{5-n}\text{H}_n\text{PTiW}_{11}\text{O}_{40}$ ($n=2-5$) is not due to the formation of lower nuclearity species, e.g. the Venturello complex, but is most likely due to peroxo species **II**, which contains two activating protons. Further spectroscopic and kinetic studies are in progress to establish the structure of **II** and detailed mechanism of its interaction with alkenes and other organic substrates.

Acknowledgements

RFBR (grant 04–03–32113) funded the research. We thank K.F. Obzherina for IR measurements.

References

- [1] R.A. Sheldon, J. Dakka, *Catal. Today* 19 (1994) 215.
- [2] B. Notari, *Adv. Catal.* 41 (1996) 253.
- [3] J.S. Rafelt, J.H. Clark, *Catal. Today* 57 (2000) 33.
- [4] M.G. Clerici, *Top. Catal.* 13 (2000) 373.
- [5] W.R. Sanderson, *Pure Appl. Chem.* 72 (2000) 1289.
- [6] D. Mandelli, M.C.A. van Vliet, R.A. Sheldon, U. Schuchardt, *Appl. Catal. A: General* 219 (2001) 209.
- [7] G. Centi, S. Perathoner, *Catal. Today* 77 (2003) 287.
- [8] G. Grigoropoulou, J.H. Clark, J.A. Elings, *Green Chem.* 5 (2003) 1.
- [9] R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* (2003) 1977.
- [10] M. Ziolek, *Catal. Today* 90 (2004) 145.
- [11] K. Sato, M. Aoki, R. Noyori, *Science* 281 (1998) 1646.
- [12] Y. Deng, Z. Ma, K. Wang, J. Chen, *Green Chem.* 1 (1999) 275.
- [13] J.-M. Bregeault, F. Launay, A. Atlamsani, C. R. Acad. Sci. Paris, *Serie Iic, Chemistry* 4 (2001) 11.
- [14] R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* (2003) 1977.
- [15] S.-O. Lee, R. Raja, K.D.M. Harris, J.-M. Thomas, B.F.G. Johnson, G. Sankar, *Angew. Chem., Int. Ed. Engl.* 42 (2003) 1520.
- [16] F. Chiker, G. Lapisardi, F. Launay, J.-F. Nogier, J.-L. Bonardet, *Catal. Commun.* 5 (2004) 247.
- [17] M.T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer Verlag, New York, 1983.
- [18] M.T. Pope, A. Müller (Eds.), *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer, Dordrecht, The Netherlands, 1993.
- [19] M.T. Pope, A. Müller (Eds.), *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*, Kluwer, Dordrecht, The Netherlands, 2001.
- [20] J.B. Moffat, *Metal-Oxygen Clusters: The Surface and Catalytic Properties of Heteropoly Oxometalates*, Kluwer/Plenum, New York, 2001.

- [21] J.J. Borrás-Almenar, E. Coronado, A. Müller, M.T. Pope (Eds.), *Polyoxometalate Molecular Science*, Kluwer, Dordrecht, The Netherlands, 2003.
- [22] C.L. Hill, C.M. Prosser-McCarthy, *Coord. Chem. Rev.* 143 (1995) 407.
- [23] R. Neumann, *Prog. Inorg. Chem.* 47 (1998) 317.
- [24] N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 199.
- [25] C.L. Hill, *Polyoxometalates: reactivity*, in: A.G. Wedd (Ed.), *Comprehensive Coordination Chemistry II*, vol.4, Elsevier Science, New York, 2004, p. 679.
- [26] R.G. Finke, B. Rapko, R.J. Saxton, P.J. Domaille, *J. Am. Chem. Soc.* 108 (1986) 2947.
- [27] Q. Chen, J. Zubieta, *Coord. Chem. Rev.* 114 (1992) 107.
- [28] T.R. Mohs, Y. Du, B. Plashko, E.A. Maatta, *Chem. Commun.* (1997) 1707.
- [29] L.C.W. Baker, D.C. Glick, *Chem. Rev.* 98 (1998) 3.
- [30] O.A. Kholdeeva, G.M. Maksimov, R.I. Maksimovskaya, L.A. Kovaleva, M.A. Fedotov, V.A. Grigoriev, C.L. Hill, *Inorg. Chem.* 39 (2000) 3828.
- [31] O.A. Kholdeeva, L.A. Kovaleva, R.I. Maksimovskaya, G.M. Maksimov, *J. Mol. Catal. A: Chem.* 158 (2000) 223.
- [32] O.A. Kholdeeva, R.I. Maksimovskaya, G.M. Maksimov, L.A. Kovaleva, *Kinet. Catal.* 42 (2001) 217.
- [33] O.A. Kholdeeva, T.A. Trubitsina, R.I. Maksimovskaya, A.V. Golovin, W.A. Neiwert, B.A. Kolesov, X. López, J.-M. Poblet, *Inorg. Chem.* 43 (2004) 2284.
- [34] C. Venturello, R. D'Aloisio, J.C.R. Bart, M. Ricci, *J. Mol. Catal.* 32 (1985) 107.
- [35] C. Venturello, R. D'Aloisio, *J. Org. Chem.* 53 (1988) 1553.
- [36] C. Venturello, M. Gambaro, *Synthesis* 1389 (1989) 295.
- [37] M. Swegler, M. Floor, H. Van Bekkum, *Tetrahedron Lett.* 29 (1988) 823.
- [38] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* 53 (1988) 3587.
- [39] R. Neumann, M. Gara, *J. Am. Chem. Soc.* 117 (1995) 5066.
- [40] R. Neumann, A.M. Khenkin, *J. Mol. Catal. A: Chemical* 114 (1996) 169.
- [41] T. Yamase, E. Ishikawa, Y. Asai, S. Kanai, *J. Mol. Catal. A: Chemical* 114 (1996) 237.
- [42] E. Ishikawa, T. Yamase, *J. Mol. Catal. A: Chemical* 142 (1999) 61.
- [43] G. Gelbard, F. Breton, M. Quenard, D.C. Sherrington, *J. Mol. Catal. A: Chemical* 153 (2000) 7.
- [44] D. Hoegaerts, B.F. Sels, D.E. de Vos, F. Verpoort, P.A. Jacobs, *Catal. Today* 60 (2000) 209.
- [45] F. Gao, T. Yamase, H. Suzuki, *J. Mol. Catal. A: Chemical* 180 (2002) 97.
- [46] M. Cohen, R. Neumann, *J. Mol. Catal. A: Chemical* 146 (1999) 291.
- [47] Y. Watanabe, K. Yamamoto, T. Tatsumi, *J. Mol. Catal. A: Chemical* 145 (1999) 281.
- [48] G. Gelbard, T. Gauducheau, E. Vidal, V.I. Parvulescu, A. Crosman, V.P. Pop, *J. Mol. Catal. A: Chemical* 182–183 (2002) 257.
- [49] A.C. Dengel, W.P. Griffith, B.C. Parkin, *J. Chem. Soc., Dalton Trans.* (1993) 2683.
- [50] L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Doremieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.-M. Brégeault, *Inorg. Chem.* 33 (1994) 871.
- [51] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, *J. Am. Chem. Soc.* 117 (1995) 681.
- [52] Y. Ding, Q. Gao, G. Li, H. Zhang, J. Wang, L. Yan, J. Suo, *J. Mol. Catal. A: Chemical* 218 (2004) 161.
- [53] O.M. Kulikova, R.I. Maksimovskaya, S.M. Kulikov, I.V. Kozhevnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 8 (1991) 1726.
- [54] G.M. Maksimov, R.I. Maksimovskaya, I.V. Kozhevnikov, *Zh. Neorgan. Khim.* 37 (1992) 2279.
- [55] O.A. Kholdeeva, T.A. Trubitsina, M.N. Timofeeva, G.M. Maksimov, R.I. Maksimovskaya, V.A. Rogov, *Inorg. Chem.*, in press.
- [56] M.N. Timofeeva, *Appl. Catal. A: General* 256 (2003) 19.
- [57] V. Stephane, E. Horst, *Liebigs Ann. Recl.* (1997) 2567.
- [58] H. Elias, S. Vayssie, *Mechanistic and preparative aspects of oxygen transfer*, in: W. Adam (Ed.), *Peroxide Chemistry*, Wiley-VCH, Weinheim, 2000, p. 131.
- [59] M.G. Clerici, *Appl. Catal. A: General* 68 (1991) 249.
- [60] G. Bellussi, A. Cazati, M.G. Clerici, G. Maddinelli, R. Millini, *J. Catal.* 133 (1992) 220.
- [61] M.G. Clerici, P. Ingallina, *J. Catal.* 140 (1993) 71.
- [62] B. Notari, *Adv. Catal.* 41 (1996) 253.
- [63] R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- [64] K.A. Jorgensen, *Chem. Rev.* 89 (1989) 431.
- [65] G.M. Maksimov, L.I. Kuznetsova, K.I. Matveev, R.I. Maksimovskaya, *Koord. Khim.* 11 (1985) 1353 (in Russian).
- [66] T. Yamase, T. Ozeki, S. Motomura, *Bull. Chem. Soc. Jpn.* 65 (1992) 1453.
- [67] O.A. Kholdeeva, M.P. Vanina, M.N. Timofeeva, R.I. Maksimovskaya, T.A. Trubitsina, M.S. Melgunov, E.B. Burgina, J. Mrowiec-Białoń, A.B. Jarzębski, C.L. Hill, *J. Catal.* 226 (2004) 363.
- [68] V.W. Day, W.G. Klemperer, D.J. Maltbie, *J. Am. Chem. Soc.* 109 (1987) 2991.
- [69] X. López, C. Bo, J.M. Poblet, *J. Am. Chem. Soc.* 124 (2002) 12574.