ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 6, pp. 816–822. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © B.G. Donoeva, T.A. Trubitsyna, G. Al-Kadamany, U. Kortz, O.A. Kholdeeva, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 6, pp. 843–849.

VIII INTERNATIONAL CONFERENCE ON MECHANISMS OF CATALYTIC REACTIONS

Catalytic Properties of the Polyoxometalate $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ in Selective Oxidations with Hydrogen Peroxide

B. G. Donoeva[a], T. A. Trubitsyna[a], G. Al-Kadamany[b], U. Kortz[b], and O. A. Kholdeeva[a]

[a] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

[b] *Jacobs University, School of Engineering and Science, Bremen, Germany*

e-mail: khold@catalysis.ru

Received December 30, 2009

Abstract—The catalytic properties of the sandwich polyoxometalate $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$, which contains two ($B$-α-$As^{III}W_9O_{33}$) fragments linked together by a "belt" consisting of one octahedral $WO(H_2O)^{4+}$ and two square-pyramidal $Ti(OH)^{3+}$ groups, have been investigated in the selective liquid-phase oxidation of organic compounds by aqueous hydrogen peroxide. The polyoxometalate shows high catalytic activity and selectivity in the oxidation of alkenes, alcohols, diols, and thioethers. The composition of the reaction products indicates that hydrogen peroxide is activated via a heterolytic mechanism.

DOI: 10.1134/S0023158410060066

Titanium-containing catalysts have attracted wide attention owing to their capability to convert organic substrates into oxygen-containing products under the action of hydrogen peroxide, an environmentally friendly oxidizer [1, 2]. In the early 1980s, Enichem Ltd. synthesized microporous titanium silicate (TS-1) having the unique capacity to activate hydrogen peroxide and to catalyze the oxidation of small substrate molecules (<0.6 nm) via a heterolytic mechanism [3]. Many research groups have been engaged in developing a mesoporous analogue of TS-1 applicable to the oxidation of large molecules [4, 5]. However, most of the presently known mesoporous titanium silicates differ markedly in catalytic properties from TS-1: their action in the oxidation of organic compounds by hydrogen peroxide is characterized by an appreciable contribution from homolytic routes [6]. The causes of this difference in catalytic action between the titanium silicates are not quite clear and remain a subject of extensive discussion.

Although considerable progress in the understanding of the nature of the activity of TS-1 and other titanium-containing catalysts has been made through experimental and theoretical studies [6–8], there is still much to be learned about the structure of active sites in these catalysts and about the chemical interactions at the molecular level. Since reactive intermediates are often easier to detect and identify in solution than in the solid phase, increasingly greater attention is being focused on mechanisms of catalysis by homogeneous model systems [9, 10]. Investigation of the catalytic properties of soluble titanium-containing compounds with different structures could shed light on H_2O_2 activation by various types of Ti sites. However, titanium complexes with organic ligands are prone to oxidative and hydrolytic destruction and, therefore, cannot be used in the study of hydrogen peroxide activation. By contrast, titanium-substituted metal oxide clusters (polyoxometalates, POMs) are inorganic in nature and are thermodynamically stable to oxidation and hydrolysis in a wide pH range. This makes them suitable molecular models for studying Ti sites in the presence of aqueous H_2O_2 [11, 12].

It was demonstrated earlier that the catalytic properties of $[PTi(OH)W_{11}O_{39}]^{4-}$, a titanium-monosubstituted heteropolyoxotungstate with a Keggin structure, and its derivatives (Ti-POMs) are similar to the properties of hydrophilic mesoporous titanium silicate catalysts in the oxidation of alkenes, thioethers, and alkylphenols with hydrogen peroxide [12]. The lacunary fragment $PW_{11}O_{39}^{7-}$ in the Ti-POMs serves as a pentadentate ligand for the hexacoordinated titanium ion, which is strongly bonded with the four nearest-neighbor tungsten atoms and with the central phosphorus atom through bridging oxygen atoms (Fig. 1a). Only the outer coordination site of titanium is labile and can interact with reactants during a catalytic process. It was established that these octahedrally coordinated, isolated titanium ions catalyze oxidation reactions mainly via the homolytic mechanism and cannot carry out the heterolytic transfer of an oxygen atom from the hydrogen peroxide molecule to the organic substrate [11, 12].

The titanium-substituted sandwich polyoxometalate $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**) has been synthesized and comprehensively characterized in a

recent study [13]. This polyanion consists of two Keggin fragments (B-α-$As^{III}W_9O_{33}$) linked together by two square pyramidal $[Ti(OH)]^{3+}$ groups and one octahedral $[WO(H_2O)]^{4+}$ fragment (Fig. 1b). The specific location of the TiOH groups in **1** prevents the formation of intramolecular and intermolecular Ti–O–Ti bonds. The unusual coordination environment of the titanium atoms makes **1** an interesting object for investigation of its catalytic properties and hydrogen peroxide activation mechanisms in oxidation reactions. Here, we present a comparative study of the catalytic properties of **1**, its titanium-free structural analogue $[As_2W_{21}O_{67}(H_2O)]^{6-}$ (**2**), the Keggin-type titanium-monosubstituted POM $[(PTiW_{11}O_{39})_2O]^{8-}$, and the titanium cluster–containing POMs $[(Ti_3PW_9O_{37}(OH))_3(PO_4)]^{15-}$ and $[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]^{17-}$ in the selective liquid-phase of organic compounds (alkenes, alcohols, diols, and thioethers) by aqueous hydrogen peroxide.

EXPERIMENTAL

Acetonitrile, cyclohexene, cyclohexene epoxide, *trans*-1,2-cyclohexanediol, tetra-*n*-butylammonium hydroxide (TBAOH, 0.8 mol/l solution in MeOH), and other organic chemicals were purchased from Aldrich. The TBAOH concentration was determined by titration with 1.0 M HCl. The hydrogen peroxide concentration in the initial reactant (~30 wt %) was determined by iodometric titration immediately before use. The synthesis of an aqueous solution of the potassium salt of $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (K-**1**) was described elsewhere [13]. Tetra-*n*-butylammonium salts of **1** containing different numbers of protons in the cationic moiety (H_2-**1** and $H_{0.5}$-**1**) were prepared by adding excess solid TBABr to a fresh solution of K-**1** at pH 2.1 and 2.7, respectively. In the latter case, pH was adjusted to the indicated level by adding NaOH. The pale yellow precipitates resulting from the addition of TBABr were separated by centrifugation, washed with water, and dried at 50°C. Potentiometric titration with a methanolic solution of TBAOH proved the presence of 2 and 0.5 acidic protons in H_2-**1** and $H_{0.5}$-**1**, respectively. Thermogravimetric analysis data indicated the presence of 5.5 TBA cations in the molecules of both compounds. Based on elemental analysis data, the formulas $TBA_{5.5}K_{0.5}H_2[Ti(OH)_2As_2W_{19}O_{67}(H_2O)]$ and $TBA_{5.5}Na_{1.5}K_{0.5}H_{0.5}[Ti(OH)_2As_2W_{19}O_{67}(H_2O)]$ were assigned to the compounds H_2-**1** and $H_{0.5}$-**1**, respectively [14]. The IR spectra of H_2-**1** and $H_{0.5}$-**1** are identical (KBr, 550–1200 cm^{-1}): 966 (W–O_d), 894 (W–O_b–W), 813 (Ti–O), 767 (W–O_c–W), 718 (W$_e$–O).

The polyoxometalate $[As_2W_{21}O_{69}]^{6-}$ (**2**) was synthesized via a procedure described by Leyrie et al. [15]. The TBA salt of $[As_2W_{21}O_{69}]^{6-}$ (TBA-2) was obtained by precipitation using TBABr. IR spectrum (KBr, 550–1200 cm^{-1}): 965, 891, 770, 721.

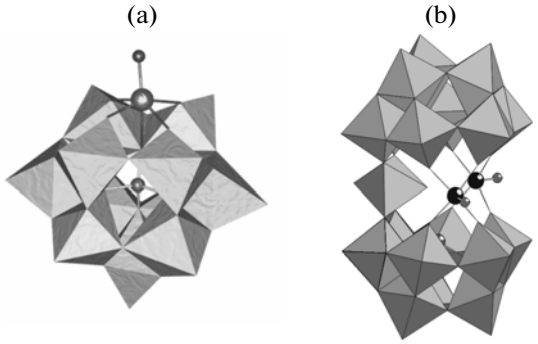


Fig. 1. (a) Monosubstituted Keggin-type polyoxometalate $[PTi(OH)W_{11}O_{39}]^{4-}$; (b) disubstituted sandwich polyoxometalate $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$.

$TBA_8[(PTiW_{11}O_{39})_2O]$ (Ti-POM), which hydrolyzes readily into the monomer $TBA_4[PTi(OH)W_{11}O_{39}]$ in the presence of water, was synthesized following an earlier reported procedure [16] (^{31}P NMR, MeCN: –13.22 ppm). The TBA-POMs $TBA_8H_7[(Ti_3PW_9O_{37}(OH))_3(PO_4)]$ (Ti_9-POM) and $TBA_{17}[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]$ (Ti_{10}-POM) were precipitated using TBABr [17]. The number of TBA cations was determined thermogravimetrically.

The TBA salt of the Venturello complex, $TBA_3\{PO_4[W(O(O_2)_2)]_4\}$ (TBA-PW_4) was obtained by the decomposition of $H_3PW_{12}O_{40} \cdot 3H_2O$ (PW_{12}) in the presence of hydrogen peroxide and orthophosphoric acid at 40°C [18].

Catalytic tests were performed in temperature-controlled glass reactors at 20–70°C in an acetonitrile medium. The reaction mixture was sampled during the reaction with a syringe and was analyzed by GC/MS and GLC using reference compounds. Quantitative analyses of the reaction products were carried out by GLC using biphenyl and dodecane as internal standards. Adipic acid was determined as its methyl ester after addition of α-methyl-α-nitrosourea to the reaction mixture [19]. The turnover frequency (TOF) was calculated from the initial substrate conversion rates.

GLC analyses were carried out on Tsvet-500 and Agilent 6890N chromatographs fitted with a flame ionization detector and a DB-5MS (30 M × 0.25 mm) and a DB-WAX (30 m × 0.25 mm) quartz capillary column, respectively. Mass spectrometric analyses were made on an Agilent 6890 chromatograph (30 m × 0.25 mm HP-ms quartz capillary column) coupled to an Agilent MSD 5973 quadrupole mass-selective detector. IR spectra were taken from sample (2 mg) + KBr (500 mg) pellets on BOMEM-MB-102 and Nicolet Avatar spectrometers. Thermogravimetric analyses were performed on a TA Instrument SDT Q600 thermobalance in flowing nitrogen (100 ml/min) in the 20–800°C range at a heating rate

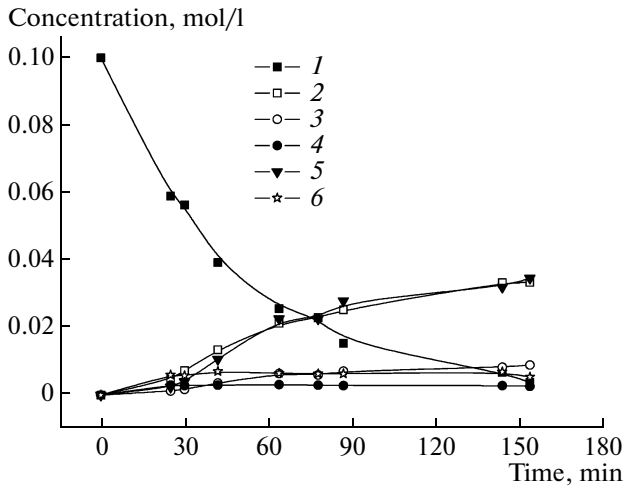


Fig. 2. Cyclohexene disappearance and oxidation product accumulation kinetics in the presence of H_2-**1**: (*1*) cyclohexene, (*2*) *trans*-1,2-cyclohexanediol, (*3*) adipic aldehyde, (*4*) 5-hydroxycaprolactone, (*5*) 2-hydroxycyclohexanone, and (*6*) cyclohexene epoxide. Reaction conditions: [cyclohexene] = 0.1 mol/l, $[H_2O_2]$ = 0.4 mol/l, [H_2-**1**] = 4×10^{-3} mol/l, 50°C, MeCN.

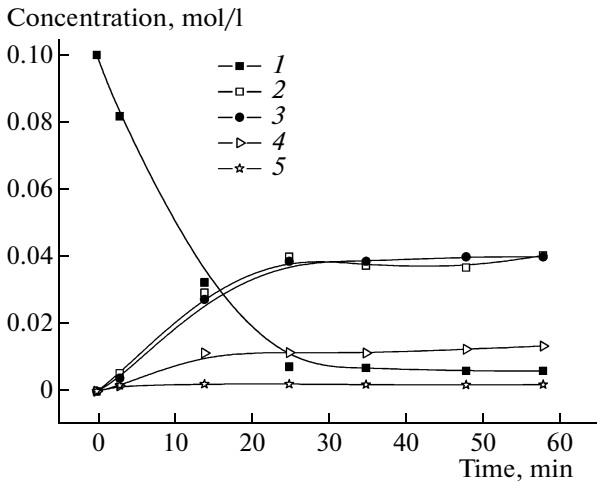


Fig. 3. Cyclohexene epoxide disappearance and oxidation product accumulation kinetics in the presence of H_2-**1**: (*1*) cyclohexene epoxide, (*2*) *trans*-1,2-cyclohexanediol, (*3*) 2-hydroxycyclohexanone, (*4*) adipic aldehyde, and (*5*) 5-hydroxycaprolactone. Reaction conditions: [epoxide] = 0.1 mol/l, $[H_2O_2]$ = 0.4 mol/l, [H_2-**1**] = 4×10^{-3} mol/l, 50°C, MeCN.

of 5 deg/min. Potentiometric titration was carried out using a Mettler-Toledo 320 pH meter.

RESULTS AND DISCUSSION

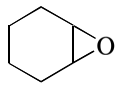
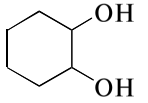
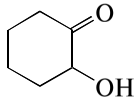
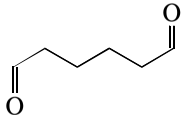
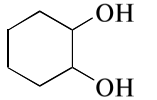
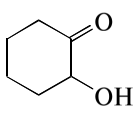
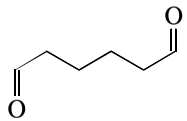
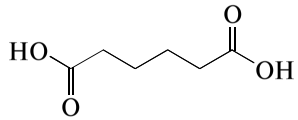
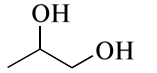
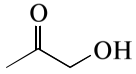
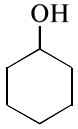
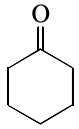
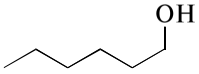
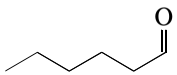
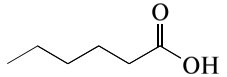
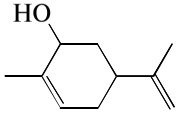
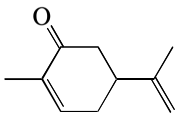
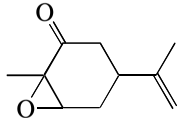
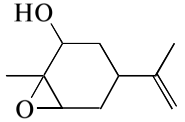
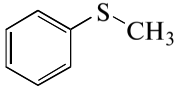
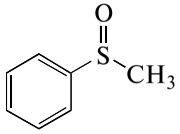
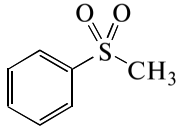
The catalytic activity of the TBA salts of **1** with different numbers of protons—$H_{0.5}$-**1** and H_2-**1**—was studied in cyclohexene oxidation with aqueous H_2O_2 in acetonitrile. It was found that the product composition depends on the amount of H^+ in the cationic moiety of the POM. In the presence of $H_{0.5}$-**1**, the major product is cyclohexene epoxide: when equimolar amounts of hydrogen peroxide and cyclohexene are reacted, the epoxide selectivity is 81% at a substrate conversion of 80% (Table 1, entry 1). The main byproducts are *trans*-1,2-cyclohexanediol and 2-hydroxycyclohexanone. Since these products result from consecutive epoxide conversion reactions, the epoxide selectivity might be expected to be higher at lower substrate conversions. The epoxide selectivity was indeed as high as 96% at a substrate conversion of 46%. The epoxide selectivity can be further increased up to 98% by lowering the reaction temperature, using a more concentrated hydrogen peroxide solution (70 wt %), and decreasing the initial H_2O_2 concentration in the reaction mixture to 0.05 mol/l. It is significant that the efficiency of use of hydrogen peroxide in cyclohexene oxidation is also high, reaching 92%.

In the presence of H_2-**1**, the epoxide yield is much lower than in the presence of $H_{0.5}$-**1** under the same conditions (Table 1, entry 2). As the oxidizer/substrate molar ratio is increased, the epoxide yield falls to an insignificant value and the amount of further oxidation products increases. This is accompanied by the appearance of 2-hydroxycyclohexanone, adipic aldehyde, 5-hydroxycaprolactone, and adipic acid among the oxidation products. The product buildup dynamics in the case of a fourfold excess of H_2O_2 over the substrate is illustrated in Fig. 2. The amount of adipic acid was measured at the end of the reaction. In 5 h, the cyclohexene conversion was 100% and the epoxide, *trans*-1,2-cyclohexanediol, 2-hydroxycyclohexanone, 5-hydroxycaprolactone, adipic aldehyde, and adipic acid yield was 4, 26, 41, 8, 9, and 9%, respectively. Note that both in the presence of H_2-**1** and in the presence of $H_{0.5}$-**1**, the allylic oxidation products—2-cyclohexen-1-ol and 2-cyclohexen-1-one—did not form even at the early stages of the reaction.

It is clear from the kinetic curves plotted in Fig. 2 that, initially, the reaction products are dominated by the epoxide and, later, *trans*-1,2-cyclohexanediol, 2-hydroxycyclohexanone, and adipic aldehyde appear among the products. The run of the kinetic curves suggests that the epoxide can turn into the diol and directly into the hydroxyketone. This was proved by the experiment in which cyclohexene epoxide was the initial substrate. The epoxide disappearance and diol and hydroxyketone accumulation curves are presented in Fig. 3. These kinetic data suggest that the diol and hydroxyketone oxidation processes are the rate-limiting steps in cyclohexene oxidation in the system examined. This is in agreement with data of other authors [20].

The outcomes of the catalytic oxidation of vicinal diols by hydrogen peroxide in the presence of H_2-**1** are

Table 1. Catalytic oxidation of organic substrates by hydrogen peroxide in the presence of **1**

Entry	[Substrate], mol/l	$[H_2O_2]$, mol/l	[POM], ($\times 10^3$, mol/l)	T, °C	Conversion,[a] %	TOF_{Ti}^{b}, h^{-1}	Selectivity,[c] %
1	0.2	0.2	$H_{0.5}$-**1** (2)	50	80	13	81 () 4 () 3 () 2 ()
2	0.2	0.2	H_2-**1** (2)	50	70	13	21 45 17 4
3	 0.1	0.4	H_2-**1** (4)	50	50[d]	1.3	 48  9  43
4	 0.1	0.4	H_2-**1** (4)	70	35	0.9	 77 CH_3COOH 23
5	 0.1	0.4	H_2-**1** (4)	70	70[e]	3.9	 98
6	 0.1	0.4	H_2-**1** (4)	70	23	0.1	 45  55
7	 0.1	0.1	H_2-**1** (2)	50	80	14	 70  15  9
8	 0.1	0.1	H_2-**1** (2)	25	95	60	 95  5

[a] Substrate conversion in 5 h.
[b] TOF_{Ti} = (moles of substrate reacted) (moles of Ti)$^{-1}$ (time)$^{-1}$, derived from initial reaction rate data.
[c] GC yield based on substrate consumed.
[d] In the absence of a catalyst, the diol conversion is 12%.
[e] In the absence of a catalyst, the cyclohexanol conversion is 13%.

Table 2. Effect of the nature of POM on the rate and selectivity of cyclohexene oxidation by H_2O_2[a]

POM	Cyclohexene conversion, %	TOF_{Ti}[b], h^{-1}	TOF_W[c], h^{-1}	Epoxide selectivity,[d] %
No catalyst	0	–	–	–
$H_3PW_{12}O_{40}$	0	–	–	–
$TBA_6[As_2W_{21}O_{69}(H_2O)]$	0	–	–	–
$TBA_3\{PO_4[W(O(O_2)_2)]_4\}$	84	–	9	98
$TBA_8[(PTiW_{11}O_{39})_2O]$	29	3.4	0.3	20[e]
$TBA_8H_7[(Ti_3PW_9O_{37}(OH))_3(PO_4)]$	6	1.1	0.4	2[e]
$TBA_{17}[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]$	1	–	–	–
$TBA_{7.5}Na_{1.5}K_{0.5}H_{0.5}[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)$	80	13	1.4	81

[a] Reaction conditions: [cyclohexene] = 0.2 mol/l, $[H_2O_2] = 0.2$ mol/l, [POM] = 2×10^{-3} mol/l, MeCN, 50°C, 5 h.
[b] TOF_{Ti} = (moles of substrate reacted) (moles of Ti)$^{-1}$ (time)$^{-1}$, derived from initial reaction rate data.
[c] TOF_W = (moles of substrate reacted) (moles of W)$^{-1}$ (time)$^{-1}$, derived from initial reaction rate data.
[d] GC yield based on substrate consumed.
[e] Major reaction products: 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and *trans*-1,2-cyclohexanediol.

also presented in Table 1 (entries 3 and 4). The major products of trans-1,2-cyclohexanediol oxidation are 2-hydroxycyclohexanone and adipic acid. At low substrate conversions, the reaction products are dominated by 2-hydroxycyclohexanone. 1,2-Propanediol oxidizes into hydroxyacetone and a minor amount of acetic acid.

The catalytic properties of H_2-**1** were studied in the oxidation of two alcohols, namely, cyclohexanol and hexan-1-ol (Table 1, entries 5, 6). In the case of a fourfold excess of H_2O_2, cyclohexanol turns into cyclohexanone with 98% selectivity at a substrate conversion of 70%. Cyclohexanone does not oxidize under the conditions examined: in 5 h, its conversion at 70°C is close to zero. Hexan-1-ol as a substrate is much less reactive than cyclohexanol. The main products of its oxidation are hexanal and hexanoic acid. Even at low substrate conversions (below 10%), the proportion of the carboxylic acid among the products is rather large. Thus, the catalytic properties of **1** differ markedly from those of the Ishii system (PW_{12}/H_2O_2, two phases), for which the major oxidation product of a primary alcohol is an aldehyde [18].

The oxidation of carveol, an unsaturated alcohol, in the presence of H_2-**1** yields the unsaturated ketone carvone as the major product. The main by-products in this case are the *trans* isomer of carvone epoxide and carveol epoxides (Table 1, entry 7). Note that, with the Ishii system, the oxidation of the unsaturated alcohol 2-cyclohexen-1-ol yielded an epoxide/unsaturated ketone = 2 : 1 mixture [18].

Methyl phenyl sulfide (MPS) in the presence of H_2-**1** is oxidized by one equivalent of H_2O_2 into methyl phenyl sulfoxide (MPSO) with 95% selectivity at a substrate conversion of 95% (Table 1, entry 8). This is accompanied by the formation of a small amount of methyl phenyl sulfone, the sulfoxide oxidation product. A similar result was obtained for $H_{0.5}$-**1**.

Note that the rates of the above reactions in air and in an inert (argon) atmosphere are equal. Therefore, the only actual oxidizer in the system is hydrogen peroxide, while dioxygen is uninvolved in the oxidation processes.

It is well known at present that the catalytic activity of the PW_{12}/H_2O_2 system is due to its solvolytic destruction yielding low-nuclearity tungsten peroxo complexes, among which the Venturello complex $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ (PW_4) is the most active [21]. It was hypothesized that the destruction stability of a POM should increase with an increasing charge of the polyanion, so sandwich POMs were expected to be more stable than PW_{12} [22]. It was proved by IR spectroscopy that **1** is stable in contact with a 100-fold excess of hydrogen peroxide [13]. Note that, under the conditions used in this study (MeCN, 25–70°C, $[H_2O_2]/[POM] = 100$), the heteropoly acid PW_{12} is also stable to solvolytic destruction. This was demonstrated by ^{31}P NMR spectroscopy: only the initial signal at 14.5 ppm and no new resonances were observed over 1 day after adding H_2O_2 to a solution of PW_{12} in MeCN. This is the reason why alkenes and alcohols are not oxidized by hydrogen peroxide in the presence of PW_{12} under the conditions examined (Tables 2, 3).

We made a direct comparison between the catalytic properties of TBA-**1** and TBA-PW_4 in the oxidation of cyclohexene (Table 2) and cyclohexanol (Table 3). The TOF values derived from the initial reaction rates and normalized to the number of W atoms in the polyanion demonstrate that, as compared to **1**, PW_4 is approximately 6 times more active in cyclohexene epoxidation and is 3 times more active in cyclohexanol oxidation. Under identical conditions, the cyclohexene epoxide yield is higher for PW_4, while the cyclo-

Table 3. Effect of the nature of POM on the rate and selectivity of cyclohexanol oxidation by H_2O_2[a]

POM	Cyclohexanol conversion, %	TOF_{Ti}[b], h^{-1}	TOF_{W}[c], h^{-1}	Cyclohexanone selectivity,[d] %
No catalyst	13	–	–	–
$H_3PW_{12}O_{40}$	0	–	–	–
$TBA_6[As_2W_{21}O_{69}(H_2O)]$	30	–	0.1	90
$TBA_3\{PO_4[W(O(O_2)_2)]_4\}$	57	–	1.2	98
$TBA_8[(PTiW_{11}O_{39})_2O]$	25	1.3	0.1	65
$TBA_{17}[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]$	4	–	–	–
$TBA_{5.5}K_{0.5}H_2[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]$	70	3.9	0.4	98

[a] Reaction conditions: [cyclohexanol] = 0.1 mol/l, $[H_2O_2] = 0.4$ mol/l, $[POM] = 4 \times 10^{-3}$ mol/l, MeCN, 70°C, 5 h.
[b, c, d] See Table 2.

hexanone yield with this catalyst is lower because of the low cyclohexanol conversion, which is most likely due to the rapid deactivation of PW_4 under the reaction conditions. In addition, MPS oxidation in the presence of the Venturello complex yields 83% sulfoxide and 17% sulfone at a substrate conversion of 85%. This is substantially different from what is observed for MPS oxidation in the presence of **1**, in which a higher sulfoxide selectivity is attained at a higher substrate conversion (Table 1, entry 8). Thus, the totality of data obtained in this study suggests that the catalytic properties of **1** are not due to the formation of low-nuclearity tungsten peroxo complexes.

It is significant that the presence of titanium atoms in the "belt" of compound **1** is a necessary condition for the compound to be catalytically active. Its structural analogue $TBA_6[As_2W_{21}O_{67}(H_2O)]$ (**2**), which contains no titanium atoms, is absolutely inactive in cyclohexene oxidation (Table 2). In cyclohexanol oxidation, the activity and selectivity of **2** are much lower than those of **1** (Table 3). Thus, the tungsten atoms in the "belt" of the sandwich POM are incapable of catalyzing alkene oxidation by hydrogen peroxide, but they can show some activity in the oxidation of secondary alcohols. The inactivity of PW_{12} in both reactions indicates that the tungsten atoms in Keggin fragments are not responsible for catalysis in the oxidation of alkenes and alcohols by hydrogen peroxide.

The catalytic properties of TBA-**1** differ markedly from those of the monosubstituted compound Ti_n-POM and from those of Ti_9-POM and Ti_{10}-POM, whose titanium atoms are linked by oxygen bridges [17]. It is clear from the TOF data normalized to the number of titanium atoms (Table 2) that the cyclohexene oxidation rate decreases in the order **1** ⩾ Ti-POM > Ti_9-POM > Ti_{10}-POM. For all POMs but **1**, the epoxide selectivity is not high and large amounts of the allylic oxidation products 2-cyclohexen-1-ol and 2-cyclohexen-1-one are observed along with *trans*-1,2-cyclohexanediol. This product composition is evidence that cyclohexene oxidation takes place via a homolytic mechanism in the presence of Ti_n-POM. Earlier, this was demonstrated for monosubstituted Ti-POMs [12].

We studied H_2O_2 decomposition in the presence of a number of titanium-substituted POMs in the absence of any organic substrate. It was established that the rate of this reaction normalized to the number of titanium atoms decreases in the order Ti_{10}-POM > Ti-POM > **1** (Fig. 4). This does not correlate with the order of catalytic activities of these POMs in the selective oxidation reactions. It is interesting that Ti_{10}-POM is very active in H_2O_2 decomposition and is almost inactive in the oxidation of cyclohexene and cyclohexanol by hydrogen peroxide (Tables 2, 3).

Since the titanium atoms in Ti-POM and Ti_n-POM are in an octahedral environment, it can be assumed

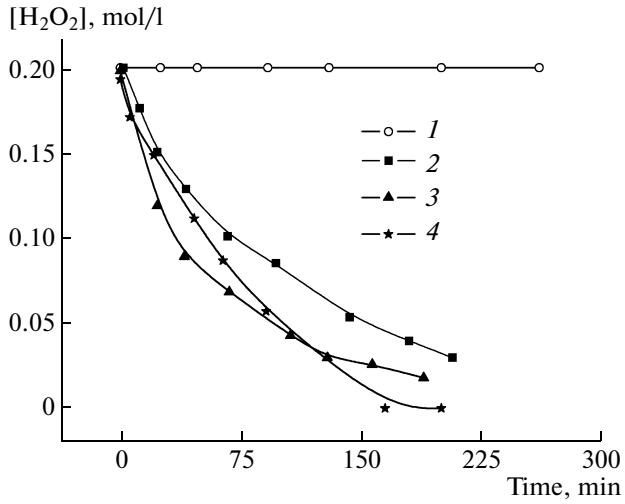


Fig. 4. Kinetics of H_2O_2 decomposition (*1*) without a catalyst and in the presence of (*2*) H_2-**1**, (*3*) $TBA_{17}[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]$, and (*4*) $TBA_8[(PTiW_{11}O_{39})_2O]$. Reaction conditions: [Ti] = 0.008 mol/l, $[H_2O_2] = 0.2$ mol/l, 70°C, MeCN.

that the unique capability of **1** to activate hydrogen peroxide via the heterolytic mechanism is due to the specific coordination number (5) and coordination geometry (square pyramidal) of the titanium atoms in this polyanion.

Thus, it has been demonstrated that the sandwich-type 19-tungstodiarsenate(III) $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ (**1**), which contains two square-pyramidal $Ti(OH)^{3+}$ groups in its "belt," is catalytically very active in the oxidation of various organic substrates by aqueous hydrogen peroxide. In alkene oxidation reactions, selectivity depends strongly on the number of protons in the cationic moiety of **1**, which can be controlled by varying the TBA salt precipitation pH. In the presence of $H_{0.5}$-**1**, cyclohexene epoxide forms with near-100% selectivity under optimum conditions. In the presence of H_2-**1**, the epoxide turns rapidly into a diol, α-hydroxyketone, and products of C–C bond breaking. No allylic oxidation products form even at the early stages of the reaction. Vicinal diols oxidize into α-hydroxyketones and (di)carboxylic acids; secondary alcohols turn into ketones with high selectivity. Primary alcohols oxidize into aldehydes and the corresponding carboxylic acids. Thioethers turn selectively into sulfoxides. The set of oxidation products suggests that **1** activates H_2O_2 and oxidizes the organic substrates mainly via a heterolytic mechanism. Thus, the catalytic properties of **1** are similar to those of the titanium silicate TS-1 (without the steric hindrance in zeolite pores taken into account) and differ markedly from those of the monosubstituted and polysubstituted POMs having octahedrally coordinated titanium atoms, for which the oxidation reactions involving H_2O_2 occur via a homolytic mechanism. The unique behavior of **1** is likely due to the specific coordination environment of the titanium atoms in the polyanion.

ACKNOWLEDGMENTS

We are grateful to Prof. E. Cadot (Versailles Saint-Quentin-en-Yvelines University, France) for providing a Ti_{10}-POM sample and to V.A. Utkin (Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences) for assistance in the identification of reaction products by the GC/MS method. We thank the Department of Physical Chemistry of Novosibirsk State University for giving us the opportunity to use an Agilent 6890N chromatograph in this study.

This work was supported by the Russian Foundation for Basic Research (grant no. 09-03-91333) and by Deutsche Forschungsgemeinschaft (DFG, grant no. KO 2288/9-1).

REFERENCES

1. Notari, B., *Adv. Catal.*, 1996, vol. 41, p. 253.
2. Thomas, J.M. and Raja, R., *Top. Catal.*, 2006, vol. 40, p. 3.
3. Clerici, M.G., *Proc. DGMK/SCI Conf. "Oxidation and Functionalisation: Classical and Alternative Routes and Sources,"* Milan, 2005, p. 165.
4. Tanev, P.T., Chibwe, M., and Pinnavaia, T.J., *Nature*, 1994, vol. 368, p. 321.
5. Corma, A., Domine, M., Gaona, J.A., Jorda, J.L., Navarro, M.T., Rey, F., Perez-Pariente, J., Tsuji, J., McCulloch, B., and Neneth, L.T., *Chem. Commun.*, 1998, p. 2211.
6. Ratnasamy, P., Srinivas, D., and Knozinger, H., *Adv. Catal.*, 2004, vol. 48, p. 1.
7. Barker, C.M., Gleeson, D., Kaltsoyannis, N., Catlow, C.R.A., Sankar, G., and Thomas, J.M., *Phys. Chem. Chem. Phys.*, 2002, vol. 4, p. 1228.
8. Yudanov, I.V., Gisdakis, P., Di Valentin, C., and Rosch, N., *Eur. J. Inorg. Chem.*, 1999, vol. 12, p. 2135.
9. Edelmann, F.T., *Angew. Chem., Int. Ed. Engl.*, 1992, vol. 31, p. 586.
10. Fandos, R., Otero, A., Rodriguez, A., Ruiz, M.J., and Trreros, P., *Angew. Chem., Int. Ed. Engl.*, 2001, vol. 40, p. 2884.
11. Kholdeeva, O.A., *Top. Catal.*, 2006, vol. 40, p. 229.
12. Kholdeeva, O.A. and Maksimovskaya, R.I., *J. Mol. Catal. A: Chem.*, 2007, vol. 262, p. 7.
13. Hussain, F., Bassil, B.S., Kortz, U., Kholdeeva, O.A., Timofeeva, M.N., de Oliveira, P., Keita, B., and Nadjo, L., *Chem. Eur. J.*, 2007, vol. 13, p. 4733.
14. Kholdeeva, O.A., Donoeva, B.G., Trubitsina, T.A., Al-Kadamany, G., and Kortz, U., *Eur. J. Inorg. Chem.*, 2009, p. 5134.
15. Leyrie, M., Martin-Frère, J., and Hervé, G., *C. R. Acad. Sci.*, 1974, vol. 279, p. 895.
16. Kholdeeva, O.A., Trubitsina, T.A., Maksimov, G.M., Golovin, A.V., and Maksimovskaya, R.I., *Inorg. Chem.,* 2005, vol. 44, p. 1635.
17. Al-Kadamany, G., Hussain, F., Mal, S.S., Dickman, M.H., Leclerc-Laronze, N., Marrot, E., Cadot, E., and Kortz, U., *Inorg. Chem.,* 2008, vol. 47, p. 8574.
18. Ishii, Y., Yamawaki, K., Ura, T., Yamada, H., Yoshida, T., and Ogawa, M., *J. Org. Chem.*, 1988, vol. 53, p. 3587.
19. Bartsch, R.C., Miller, F.D., and Trent, F.M., *Anal. Chem.,* 1960, vol. 32, p. 1101.
20. Lee, S.O., Raja, R., Harris, K.D.M., Tomas, J.M., Johnson, B.F.J., and Sankar, G., *Angew. Chem., Int. Ed. Engl.*, 2003, vol. 42, p. 1520.
21. Aubry, C., Chottard, G., Platzer, N., Bregeault, J.-M., Rhouvenot, R., Chauveau, F., Huet, C., and Ledon, H., *Inorg. Chem.,* 1991, vol. 30, p. 4407.
22. Neumann, R., *Prog. Inorg. Chem.*, 1998, vol. 47, p. 317.