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Oxidation of Reactive Alcohols with Hydrogen Peroxide Catalyzed by Manganese Complexes

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Abstract Two manganese-containing catalysts have been employed in the oxidation with hydrogen peroxide of two reactive alcohols (1-phenylethanol and glycerol): soluble catalyst $[LMn(\mu\text{-}O)_3MnL](PF_6)_2$ (**1a**) and heterogenized catalyst $[LMn(\mu\text{-}O)_3MnL]_2[SiW_{12}O_{40}]$ (**1b**) (L is 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN). Oxidation of 1-phenylethanol catalyzed by **1a** in acetonitrile solution proceeds at room temperature in the presence of a small amount of oxalic acid; the turnover number attains 15,000 after 3 h. It has been proposed on the basis of the kinetic study that an oxidizing species is a manganyl species containing fragment "Mn=O" rather that hydroxyl radical. This species reacts competitively with the alcohol, acetonitrile and hydrogen peroxide. In the case of **1b** dependences of the initial rates of acetophenone accumulation on concentration of the alcohol and amount of **1b** have plateau. Both homogeneous and heterogeneous catalysts are efficient in the oxidation of glycerol to produce dihydroxyacetone (DHA) as the main product. The oxidation catalyzed by **1a** is one of the first examples of the glycerol oxidation by a catalytic *homogeneous* system. The yield of valuable products attained 45%. The oxidation of DHA in the absence of glycerol afforded mainly glycolic acid in yield 60% based on the starting DHA. The oxidation on **1b** represents the first example of the glycerol transformation catalyzed by a *heterogenized* metal complex. Under certain conditions yields of products of deeper oxidation (glyceric, glycolic and hydroxypyruvic acids) are somewhat higher than the yield of dihydroxyacetone. Special experiments demonstrated that no leaching of active species occurs from catalyst **1b** to the solution and that this catalyst can be re-used at least four times without substantial loss of activity.

Keywords Alcohols · Glycerol · Heterogenized catalysts · Homogeneous catalysis · Manganese complexes · Renewables

This is Part 12 from the series "Oxidations by the system 'hydrogen peroxide–$[Mn_2L_2O_3]^{2+}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid'". For parts 1–11, see Refs. 70–80, respectively.

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1 Introduction

Oxidation of alcohols to the corresponding carbonyl compounds (ketones, aldehydes, carboxylic acids) catalyzed by various metal compounds is of great importance in chemical laboratories and industry (see reviews [1–6]). Air and molecular oxygen [7–14], hydrogen peroxide [15–18], *tert*-butyl hydroperoxide [19] are used in these reactions.

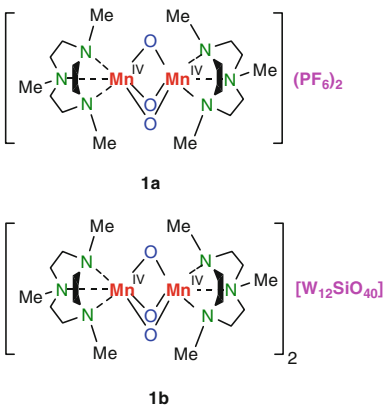
Many papers have been devoted [20–24] to the oxidation of benzyl alcohols that are the most reactive among compounds bearing hydroxyl groups and can be often oxidized by systems which are unable to transform aliphatic alcohols. Glycerol is a by-product from biodiesel

[25–27] production. Industries using fats and oils as feedstock produce fatty acids, alcohols and soap also yield glycerol as a co-product (see reviews [28–34]). Oxidative transformations of glycerol are especially important from the practical point of view [28–34]. Dihydroxyacetone (DHA) is the first product in the chain of the consecutive glycerol oxidation and this is very valuable and important compound. DHA does not damage the skin and it is widely used in cosmetics as a safe skin coloring agent (lotions, gels, mousses and wipes) as well as a nutritional supplement. This compound serves as a versatile building block for the synthesis of a variety of fine chemicals. It can affect the sensory quality of the wine with sweet/etherish property. Another primary product of glycerol oxidation, glyceric acid, in the form of phosphate derivatives is used as biochemical intermediates. Glycolic acid which is formed from glycerol *via* C–C bond rapture finds applications in skin care products, it reduces hyperpigmentation, wrinkles, acne scarring. Finally, tartronic acid formed from glycerol is oxidized to mesoxalic acid which is known as an antidote to cyanide poisoning.

A few methods of glycerol oxidation employing air or molecular oxygen have been reported. These processes use heterogeneous metal derivatives as catalysts [35–47]. Gold catalysts are especially active in the glycerol oxidation [48–54]. Some publications have been devoted to the aerobic oxidation of glycerol catalyzed by enzymes and living organisms [45–58], particularly dihydroxyacetone is produced *via* the oxidation of glycerol with the participation of bacterium *Gluconobacter oxydans* [59]. Only restricted number of papers reported metal-catalyzed heterogeneous glycerol oxidations with H_2O_2 [60–62]. Qualitative experiments on the oxidation catalyzed by iron ions have been reported [63].

Glycerol is a very reactive compound and usually its oxidation gives rise to the formation of a variety of products. Due to the high reactivity both of glycerol and the products of its oxidation the oxidation of glycerol unfortunately affords desirable products in low yield and selectivity. Thus, for example, in the aerobic glycerol oxidation over Pt/carbon catalyst the glycerol conversion was in the interval 30–89% and the target product glyceric acid was formed with selectivity 7–47%. Mass balance determined on the bases of observed C_2 and C_3 products was <47%. Other catalyst samples gave mixtures of comparable amounts of glyceric, oxalic, tartronic acids and glyceraldehyde [36]. The oxidation of glycerol with H_2O_2 using Au/C as a catalyst was carried out with conversion 13%. A mixture of glyceric + tartronic, oxalic, hydroxypyruvic, glycolic and formic acids in the 39.3:3.5:1.2:26.1:29.9 ratio was produced [43]. Many heterogeneous catalysts lead to the predominant formation of the products of deep oxidation that are not very valuable (formic acid, formaldehyde and even CO_2). Unfortunately, DHA was either not produced at all in many aerobic heterogeneous oxidations [37, 39, 64] or its yields were very low (4%) [65]. Maximum attained yield of DHA in H_2O_2 oxidation catalyzed by Ti-containing material EP50Fd was 2% [60]. The aerobic glycerol oxidation [45] catalyzed heterogeneously by Pt/C gave with 50% conversion the following products: glyceric acid, DHA, glycolic acid, glyceraldehyde, hydroxypyruvic acid, formaldehyde + CO + CO_2 in the 47.7:17.0:13.6:2.1:2.1:17.8 ratio. The oxidation in a slurry bubble column reactor structured at the bubble scale over Au/C gave at 30% glycerol conversion a 1:1 mixture of glyceric acid and DHA in addition to smaller amounts of tartronic and oxalic acids [42]. Only in some cases the yield of DHA attained 35% by continuous aerobic glycerol oxidation on heterogeneous metallic catalysts [35, 66–68]. Bimetallic Pt–Bi catalysts [69] show a high initial selectivity to DHA in acidic media but exhibit a strong deactivation during reaction as well, which decreases activity and selectivity to dihydroxyacetone. As a result, only moderate yields may be achieved. In summary, it may be concluded that the selective oxidation of glycerol to DHA is a challenging task of contemporary catalytic chemistry. One of the main problems existing in this field is the over-oxidation of initially formed reactive products. Due to this it is very difficult to produce primary oxygenates (DHA) in appropriate yields.

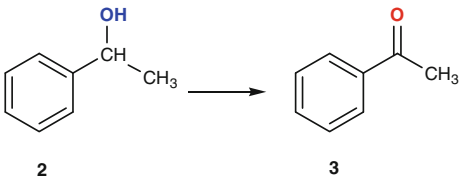
Some of us [70] discovered in 1998 that dinuclear manganese(IV) complex $[LMn(O)_3MnL](PF_6)_2$ (catalyst **1a**, where L is 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN; see Scheme 1) catalyzes the oxidation of organic compounds by hydrogen peroxide if a small amount of a carboxylic acid is added to the reaction solution. Further, we demonstrated that the '**1a**/carboxylic acid/H_2O_2' combination in acetonitrile solution very efficiently oxidizes various organic compounds [70–87] (see also reviews [88–94]) including inert alkanes [70–76, 78, 81, 82, 85–87] to afford primarily the corresponding alkyl



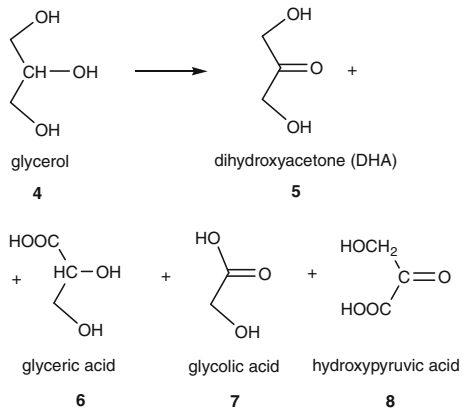
Scheme 1 Catalysts used in the present work

hydroperoxides which are transformed in the course of the reaction into the more stable ketones (aldehydes) and alcohols. It turned out that the system oxidizes not only alkanes but also epoxidizes olefins [72, 74–76, 84, 87], transforms alcohols into ketones (aldehydes) [72, 77, 83] and sulfides into sulfoxides [72]. The reaction with olefins afforded the products of dihydroxylation [74] in addition to the corresponding epoxides. Alkanes [75], olefins [76], and alcohols [77] were oxidized also in the absence of acetonitrile. A relevant soluble polymer-bound Mn(IV) complex with N-alkylated 1,4,7-triazacyclononane was used as a catalyst in the H_2O_2 oxygenation of alkanes [82]. We have also demonstrated that alkanes and olefins can be oxidized by *tert*-butyl hydroperoxide [72, 95, 96] or peroxyacetic acid [81, 97] using complex **1a** as a catalyst. The reaction with *tert*-butyl hydroperoxide is significantly accelerated in the presence of a small amount of a carboxylic acid [72, 96]. Veghini, Fischer and coworkers [98] prepared insoluble salt of formula $[LMn(\mu\text{-}O)_3MnL]_2[SiW_{12}O_{40}]$ (catalyst **1b**) which turned out to be an active catalyst in the oxidation of alcohols [77, 98] and olefins [98]. Very recently, we used catalysts **1** in a study devoted to the decoloration of dye Rhodamine 6G [80].

Continuing the studies of oxidations by our '**1**/carboxylic acid/H_2O_2' system which efficiently transforms very inert alkanes we decided to apply this system in contrast to oxidative transformations of two very reactive alcohols, namely 1-phenylethanol (**2**; see Scheme 2) and glycerol (**4**; see Scheme 3). Both alcohols can be easily oxidized by various reagents because compound **2** contains benzylic hydroxyl group, and glycerol bears three hydroxyls at secondary and primary carbon atoms. However, as the secondary alcohol **2** cannot be oxidized to aldehyde or carboxylic acid its over-oxidation is restricted. In contrast to the case of alcohol **2**, one of the main characteristic features of the glycerol oxidation is its easy over-oxidation. It is interesting to compare oxidation of compounds **2** and **4**. As our '**1a**/carboxylic acid/H_2O_2' system oxidizes organic compounds under very mild conditions (ambient or even lower temperature) we assumed that the application of this reagent to the glycerol transformation would not lead to the extensive over-oxidation to non-valuable products.



Scheme 2 Oxidation of 1-phenylethanol to acetophenone



Scheme 3 Products of glycerol oxidation

2 Results and Discussion

We have found that under the action of the homogeneous 'H_2O_2–**1a**–oxalic acid' system in acetonitrile in air at room temperature alcohol **2** is easily oxidized to produce acetophenone **3**. The kinetic curves of the **3** accumulation and **2** consumption are shown in Fig. 1 (typical conditions are given in the Figure caption). Turnover number (moles of **3** formed per one mole of catalyst **1a**, TON) attained 15,000 after 3 h which corresponds to the **3** yield 94%. Turnover frequency in the initial period was 7,400 h^{-1}. It should be noted that when the reaction was carried out under the same conditions but in an argon atmosphere the kinetic curves practically coincided with the curves shown in Fig. 1.

We carried out a detailed kinetic study of the oxidation of 1-phenylethanol and determined dependencies of the initial accumulation rate W_0 of acetophenone on the initial concentrations of each reagent. The concentrations of all

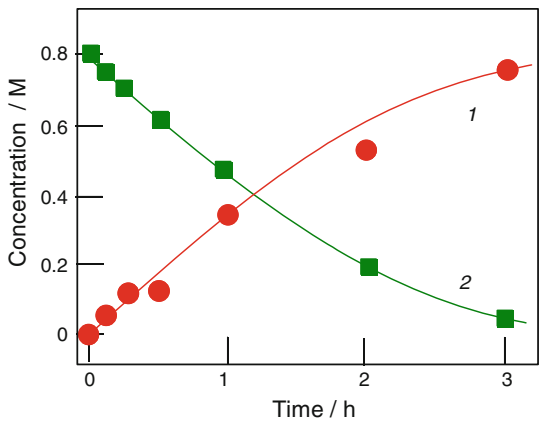


Fig. 1 Accumulation of acetophenone (curve *1*) in the oxidation of 1-phenylethanol (curve *2*; initial concentration 0.8 M) with H_2O_2 (initial concentration 4.0 M) catalyzed by complex **1a** (5×10^{-5} M) in the presence of oxalic acid (0.05 M). Solvent was acetonitrile, $[H_2O]_{total}$ = 14.2 M, 22 °C, the experiment in air

other reagents in each experiment maintained fixed. It follows from Fig. 2 that the dependence of W_0 on the initial concentration of soluble catalyst **1a** is linear at [**1a**] $< 5 \times 10^{-5}$ M. The initial oxidation rate increases with growing the concentration of co-catalyst oxalic acid (Fig. 3). However, at concentration [oxalic acid] >0.02 M the rate does not practically depend on the concentration of oxalic acid. It should be noted that unlike the oxidations of alkanes and relatively inert alcohols (for example, cyclohexanol) the oxidation of **2** occurs with noticeable rate even in the absence of an acid. Curves corresponding to dependences of W_0 on the initial concentration of substrate **2** (Fig. 4, curve *1*) and on the initial concentration of hydrogen peroxide (Fig. 5, curve *1*) are not straight lines.

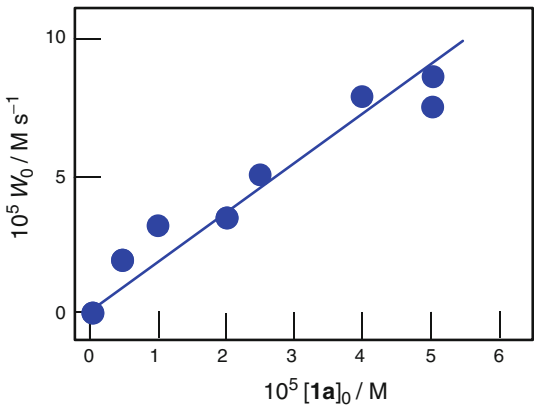


Fig. 2 Dependence of the initial rate of acetophenone accumulation W_0 in the oxidation of 1-phenylethanol on the initial concentration of catalyst **1a**. Conditions: [1-phenylethanol]$_0$ = 0.8 M, [H_2O_2]$_0$ = 4.0 M, [oxalic acid]$_0$ = 0.05 M, [H_2O]$_{total}$ = 14.2 M; 22 °C

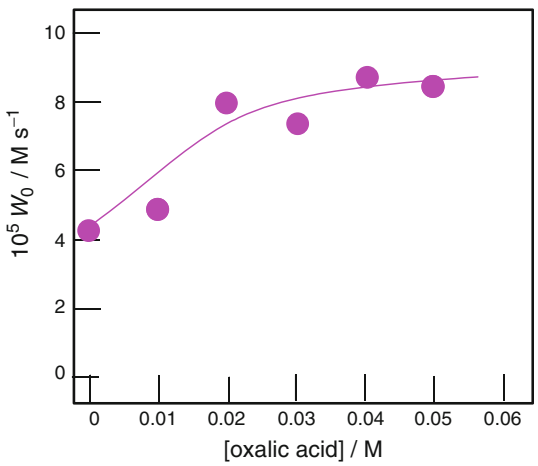


Fig. 3 Dependence of the initial rate of acetophenone accumulation in the homogeneously catalyzed oxidation of 1-phenylethanol on the concentration of oxalic acid. Conditions: [1-phenylethanol]$_0$ = 0.8 M, [H_2O_2]$_0$ = 4.0 M, [**1a**]$_0$ = 5×10^{-5} M, [H_2O]$_{total}$ = 14.2 M, 22 °C

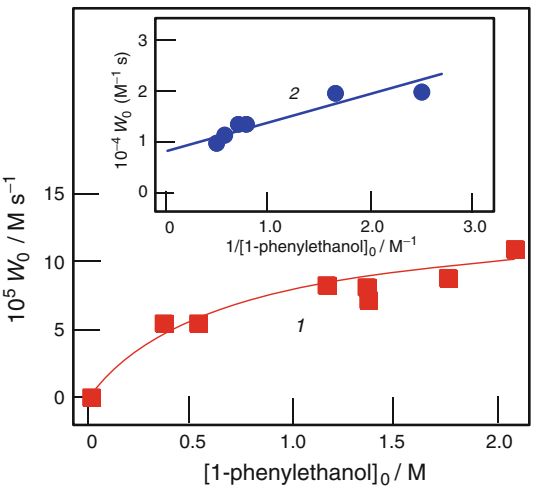


Fig. 4 Dependence of the initial rate of acetophenone accumulation in the oxidation of 1-phenylethanol on the initial concentration of 1-phenylethanol. Conditions: [H_2O_2]$_0$ = 0.5 M, [**1a**]$_0$ = 2.5×10^{-5} M, [oxalic acid] = 0.05 M, [H_2O]$_{total}$ = 3.55 M, 22 °C. Curve *2* is the linearization of the data presented with curve *1* using coordinates 1/[1-phenylethanol]$_0$ − 1/W_0

The obtained kinetic data allow us to discuss a possible mechanism of the reaction and the nature of the oxidizing species. First of all, it is necessary to note that the kinetic curves of the alcohol **2** consumption and ketone **3** accumulation shown in Fig. 1 indicate that the ketone is formed in the yield higher than 90% based on the oxidized alcohol. Such a high selectivity of the transformation **2** → **3** could not be noticed in the case of the oxidation with the participation of hydroxyl radicals. At least two facts allow us to assume this. First, the analysis of the data taken from the literature [99–101] demonstrates that the probability of the interaction of the hydroxyl radical with phenyl ring of **2** is higher than with the OH group of this alcohol. Due to this a considerable amount of the products of the oxidative transformation of the phenyl fragment (hydroxylation etc.) could be formed in addition to the main product **3**. In this case the 90% conversion of **2**–**3** would be unlikely. Second, the rate constants of the hydroxyl radical interaction with compounds **2** and **3** are close to 1.3×10^{10} and 5.5×10^{9} M^{-1} s^{-1}, respectively [99–101]. Therefore, in the sequence of transformations '**2** → **3** → products of deeper oxidation' which is induced by HO$^{\bullet}$ radicals the maximum attained concentration of compound **3** in the oxidation of 0.8 M of **2** must not be higher than 0.55 M. This concentration corresponds to the 70% conversion of **2**–**3** which is substantially lower than the conversion obtained in our experiments. We may conclude that hydroxyl radicals are not main oxidizing species in our system.

The data presented in Figs. 4 and 5 give an additional support for our hypothesis about the nature of the oxidizing

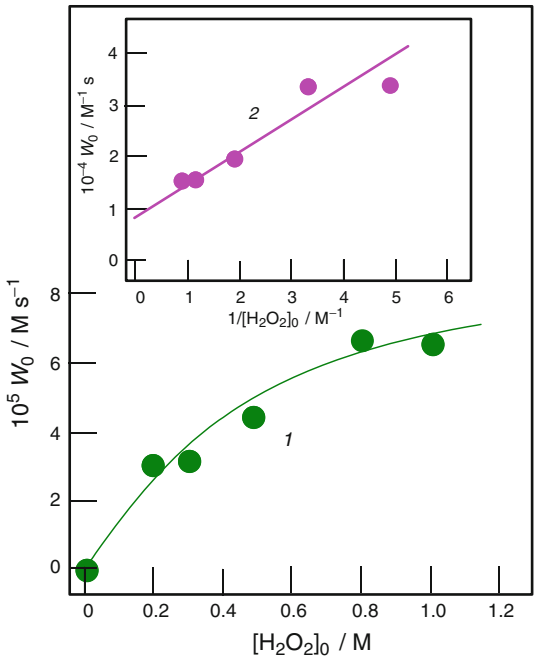


Fig. 5 Dependence of the initial rate of acetophenone accumulation W_0 in the oxidation of 1-phenylethanol on the initial concentration of hydrogen peroxide at constant total concentration of water. Conditions: $[1\text{-phenylethanol}]_0 = 0.8$ M, $[\mathbf{1a}]_0 = 2.5 \times 10^{-5}$ M, $[\text{oxalic acid}]_0 = 0.05$ M, $[H_2O]_{total} = \text{const} = 3.55$ M, 22 °C. Curve *2* is the linearization of the data presented with curve *1* using coordinates $1/[H_2O_2]_0 - 1/W_0$

species. The mode of dependence of the initial rate W_0 of acetophenone formation on initial concentration of **2** is typical for the case when a competitive interaction occurs between 1-phenylethanol and some components of the reaction mixture on the one hand and oxidizing species X on the other hand. Indeed, solvent acetonitrile and the oxidizing reagent (hydrogen peroxide) can play the role of such competitors for alcohol **2** in the reaction with X. We propose the following kinetic scheme which corresponds to the competitive oxidation of the alcohol:

$$H_2O_2 + \text{catalyst } \mathbf{1a} + \text{co-catalyst oxalic acid} \rightarrow X \quad W_i \qquad \text{(i)}$$

$$X + \text{1-phenylethanol } (\mathbf{2}) \rightarrow \text{products } k_1 \qquad (1)$$

$$X + \text{acetonitrile} \rightarrow \text{products } k_2 \qquad (2)$$

$$X + H_2O_2 \rightarrow \text{products } k_3 \qquad (3)$$

where W_i is the rate of the oxidizing species X generation by the catalytic system. When we consider this kinetic scheme we do not take into account the possibility of primary products formed in stages (1), (2), and (3) to react further with the oxidizing system.

Let us assume again that the oxidizing species in our system is hydroxyl radical (X ≡ HO$^\bullet$). In this case for the studied concentration intervals of **2** this alcohol should accept all oxidizing species X and dependence shown in Fig. 4 should not be observed. Indeed, in accordance with the literature data [99–101] under typical for our experiments conditions the pseudo-first order constants for the interactions of hydroxyl radicals with **2**, MeCN and H_2O_2 are equal to $k_1[\mathbf{2}] = 1.3 \times 10^{10} \cdot 0.4 = 5.2 \times 10^9$ s^{-1}, $k_2[\text{MeCN}] \leq 2.2 \times 10^8 \cdot 18 = 4 \times 10^8$ s^{-1} and $k_3[H_2O_2] = 4 \times 10^7 \cdot 0.5 = 2 \times 10^7$ s^{-1}, respectively. Since under conditions of our experiments value $k_1[\mathbf{2}]$ is much higher than $k_2[\text{MeCN}]$ and $k_3[H_2O_2]$ more than 90% of generated hydroxyl radicals would react with **2** and no dependence of the acetophenone accumulation rate on $[\mathbf{2}]_0$ would be noticed.

Assuming that the dependence shown in Fig. 5 (curve *1*) reflects the competition between reactions (1) and (3) we can expect that the analysis of dependencies presented in Fig. 4 (curve *1*) and Fig. 5 (curve *1*) will lead to the congruous values for the kinetic parameters, namely the ratio of constants k_1 and k_3 for reactions (1) and (3). We can say that hydrogen peroxide is a trap for the active oxidizing species. We have for the case under consideration:

$$W_0 = \frac{d[3]}{dt} = \frac{W_i}{1 + \frac{k_3[H_2O_2]_0}{k_1[2]_0}} \qquad (4)$$

Assuming further that

$$W_i = k_i[\mathbf{1a}]_0[H_2O_2]_0, \qquad (5)$$

we will obtain the following expression:

$$W_0 = \frac{d[\mathbf{3}]}{dt} = \frac{k_i[\mathbf{1a}]_0[H_2O_2]_0}{1 + \frac{k_3[H_2O_2]}{k_1[\mathbf{2}]_0}} \qquad (6)$$

To describe dependencies shown in Figs. 4 and 5 (curves *1*) we have:

$$\frac{1}{W_0} = \frac{1}{k_i[\mathbf{1a}]_0[H_2O_2]_0}\left\{1 + \frac{k_3[H_2O_2]_0}{k_1[\mathbf{2}]_0}\right\} \qquad (7)$$

The linearization of the dependence presented in Fig. 4 (curve *1*) using coordinates $1/W_0$ *versus* $1/[\mathbf{2}]_0$ can be made (Fig. 4, curve *2*). The ratio of the slop angle tangent of the straight line to the segment which is cut off on Y-axes corresponds to the $k_3[H_2O_2]/k_1$ ratio. Analogously, after the linearization of the dependence presented in Fig. 5 (curve *1*) using coordinates $1/W_0$ *versus* $1/[H_2O_2]_0$ the ratio of the slope angle tangent of the straight line to the segment which is cut off on Y-axes will give us the $k_1[\mathbf{2}]/k_3$ ratio (Fig. 5, curve *2*).

The values of the kinetic parameters determined by this method are the following ones: $k_3[H_2O_2]/k_1 = 0.6$ and $k_1[\mathbf{2}]/k_3 = 0.6$. As concentration of hydrogen peroxide in the experiment of Fig. 4 is 0.5 M and concentration of **2** in the experiment of Fig. 5 is 0.8 M we will calculate $k_3/k_1 = 1.2$ from Fig. 4 and $k_1/k_3 = 0.75$ from Fig. 5. It can be seen that measured from different dependences ratios k_3/k_1

are practically the same. Indeed, Fig. 4 gives 1.2 and Fig. 5 gives 1:0.75 ≈ 1.3. This coincidence testifies that our idea on the competition of several pathways in the catalytic system is correct. Thus, we can conclude that the oxidizing species reacts with the same efficiency both with 1-phenylethanol and hydrogen peroxide, and, therefore, this species is not hydroxyl radical. It could be a manganyl species containing fragment Mn=O. High-valent metal-oxo species of such type have been previously proposed for various oxidation processes with the participation of manganese complexes [18, 73, 80, 102–108] including Mn-TACN derivatives [109–112]. In some works, the role of catalytically active bis(μ-carboxylato)-Mn_2^{III} complex has been demonstrated [113]. Low-valent manganese complexes which can be oxidized easily to higher valent derivatives have been assumed as intermediates in the epoxidation of olefins [114].

Kinetic curves of the acetophenone accumulation during first 3 h of the reaction catalyzed by the heterogenized Mn complex **1b** are shown in Fig. 6. It should be noted that when initial concentration of H_2O_2 was equal to 2.4 M (Fig. 6, curve *1*) the yield of acetophenone after 24 h was only 67%. However, if the amount of hydrogen peroxide was increased to 3.3 M (Fig. 6, curve *2*) the yield of acetophenone after 24 h attained 95%. The yield of acetophenone after 5 min reflects the initial reaction rate. Dependence of this yield on the amount of the catalyst is presented in Fig. 7. It can be seen that when the amount of **1b** > 0.6 mg/mL the initial oxidation rated does not practically depend on the amount of the heterogenized catalyst. This independence is apparently due to the aggregation of heterogeneous forms of the catalyst which leads to some contraction of the catalytically active surface. Similarly, the initial rate of 1-phenylethanol oxidation does not practically depend on initial concentration of **2** when $[\mathbf{2}]_0 > 0.3$ M (Fig. 8).

We also report here our first results on the oxidation of glycerol by the '**1**–oxalic acid–H_2O_2' system. As it has

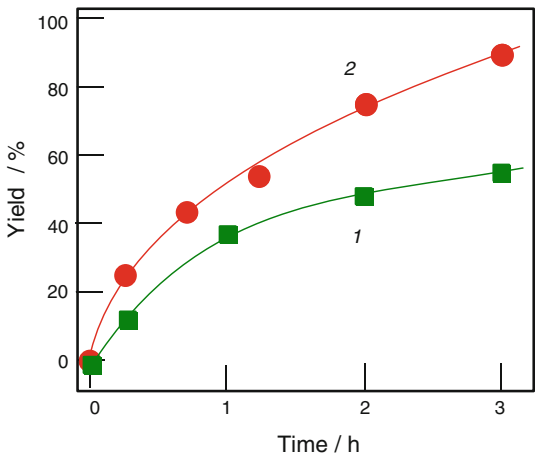


Fig. 6 Accumulation of acetophenone (yield, % based on 1-phenylethanol) in the oxidation of 1-phenylethanol (0.66 M) with H_2O_2 heterogeneously catalyzed by compound **1b** (5 mg, which is equivalent to 4.4×10^{-4} M Mn ions) in the presence of oxalic acid (0.02 M) at different concentrations of hydrogen peroxide: 2.4 M (50% aqueous, total concentration of water 4.4 M; curve *1*), 3.3 M (35% aqueous, total concentration of water 11.6 M; curve *2*). Solvent was acetonitrile, total volume of the reaction solution was 5 mL; 22 °C

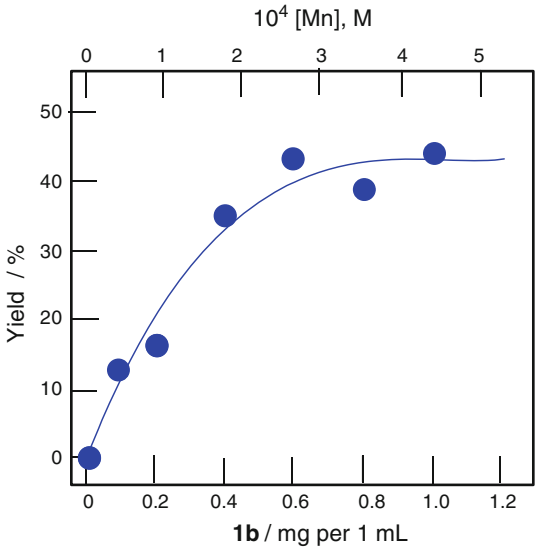


Fig. 7 Dependence of acetophenone yield (% based on 1-phenylethanol) after 5 min in the oxidation of 1-phenylethanol (0.66 M) with H_2O_2 (3.3 M; 35% aqueous, total concentration of water 11.6 M) in the presence of oxalic acid (0.02 M) on the amount of catalyst **1b** (expressed as mg per 1 mL of the solution and also as equivalent concentration of Mn ions). Solvent was acetonitrile, total volume of the reaction solution was 5 mL; 22 °C

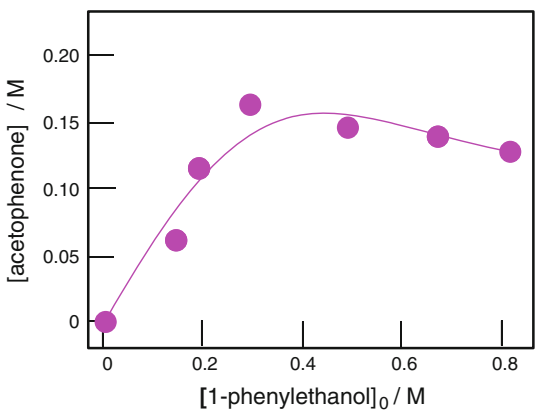


Fig. 8 Dependence of concentration of acetophenone after 5 min in the oxidation of 1-phenylethanol with H_2O_2 (3.3 M; 35% aqueous, total concentration of water 11.6 M) catalyzed by compound **1b** (5 mg, which is equivalent to 4.4×10^{-4} M Mn ions) on initial concentration of 1-phenylethanol. Solvent was acetonitrile, total volume of the reaction solution was 5 mL; 22 °C

Table 1 Oxidation of glycerol (**4**) at its relatively high initial concentration (0.5 M)

Entry	H_2O_2, M	**1a**, M	$(COOH)_2$, M	Time	**5,** mM (%)	**6,** mM (%)	**7,** mM (%)	**8,** mM (%)
1	1.0	5.0×10^{-5}	0.002	10 min	29.0 (5.8)	3.3 (0.7)	6.7 (1.3)	0 (0)
2				30 min	18.5 (4.0)	6.7 (1.3)	4.7 (0.9)	0 (0)
3				4 h	25.9 (5.2)	7.0 (1.2)	10.0 (2.0)	0 (0)
4				24 h[a]	54.0 (10.8)	26.7 (5.3)	97.0 (19.4)	0 (0)
5	1.3	5.0×10^{-5}	0.02	4 h	27.9 (5.6)	0 (0)	0 (0)	0 (0)
6				24 h	27.0 (5.5)	0 (0)	54.0 (10.0)	0 (0)
7				48 h	16.7 (3.3)	5.0 (1.0)	10.0 (2.0)	0 (0)
8	0.5	2.5×10^{-5}	0.01	10 min	16.7 (3.3)	0 (0)	0 (0)	2.0 (0.4)
9				30 min[b]	20.9 (4.2)	0.5 (0.1)	0.5 (0.1)	3.4 (0.7)
10				1 h	10.0 (2.0)	0.5 (0.1)	6.7 (1.3)	2.0 (0.4)
11	0.3[c]	5.0×10^{-5}	0	10 min	20.0 (6.7)	0.6 (0.2)	3.1 (1.0)	2.0 (0.7)
12				30 min	37.6 (12.5)	40.0 (13.6)	16.7 (5.6)	4.5 (1.5)
13				2 h	33.4 (11.1)	48.0 (15.0)	13.0 (4.0)	4.7 (1.6)
14				24 h	29.0 (9.7)	31.4 (10.5)	13.0 (4.0)	10.0 (3.4)

Conditions. Solvent was acetonitrile, total volume of the reaction solution was 5 mL, 22 °C. Yields (%) in parentheses are based on starting glycerol

[a] Glycerol conversion was 40%, mass balance was 89%

[b] Glycerol conversion was 20%, mass balance was 29%

[c] Yields were calculated based on hydrogen peroxide

been mentioned above glycerol is a very reactive alcohol and is usually oxidized to afford a variety of products. The data on the homogeneous oxidation catalyzed by **1a** under different conditions are summarized in Tables 1 and 2 (see also Scheme 3). It can be concluded that the main product usually was dihydroxyacetone. However, in some cases the products of more deep oxidation prevailed (see, for example, Table 1, entries 4, 6, 7, 10, Table 2, entries 2–5, 12). Entries 11–14 of Table 1 demonstrate that, in the oxidation of glycerol, oxalic acid is not an obligatory component of the catalytic system. The maximum yield of all valuable products attained 45% (Table 2, entry 12).

In addition, we studied the oxidation of DHA under similar conditions (Fig. 9). Unlike glycerol, DHA does not have the secondary hydroxyl groups, and in the ketonization reaction compound **5** is less reactive than **4**. Indeed, previously we demonstrated that primary alcohols are less reactive in comparison with the secondary ones in the

Table 2 Oxidation of glycerol (**4**) at its relatively low initial concentration (0.16–0.08 M)

Entry	**4,** M	**1a**, M	Time	**5**, mM (%)	**6**, mM (%)	**7**, mM (%)	**8**, mM (%)
1	0.16	5.0×10^{-5}	5 min	4.5 (2.9)	0 (0)	0 (0)	0 (0)
2			10 min	9.2 (5.9)	13.4 (8.6)	10.0 (6.5)	0 (0)
3			30 min	22.2 (14.2)	14.0 (9.1)	16.7 (10.8)	0 (0)
4			24 h[a]	23.7 (15.3)	16.7 (10.8)	16.7 (10.8)	0.8 (0.5)
5			48 h[b]	16.0 (10.0)	20.0 (12.9)	26.7 (17.2)	0.8(0.5)
6	0.16	0	24 h	0 (0)	0 (0)	0 (0)	0 (0)
7	0.16	2.5×10^{-5}	100 h	6.7 (4.3)	5.0 (3.2)	5.3 (3.4)	0 (0)
8	0.08	5.0×10^{-5}	5 min	1.8 (2.4)	0 (0)	0 (0)	0 (0)
9			10 min	3.1 (3.9)	0 (0)	0 (0)	0 (0)
10			30 min	8.0 (10.5)	4.0 (5.0)	4.0 (5.0)	0 (0)
11			1 h	9.6 (12.0)	9.0 (11.3)	9.0 (11.3)	0 (0)
12			24 h	10.0 (12.5)	12.7 (16.0)	12.7 (16.0)	0 (0)

Conditions. Solvent was acetonitrile, $[H_2O_2]_0 = 0.3$ M, $[(COOH)_2] = 0$ M, total volume of the reaction solution was 5 mL, 22 °C. Yields (%) in parentheses are based on starting glycerol

[a] Glycerol conversion was 40%

[b] Glycerol conversion was 60%

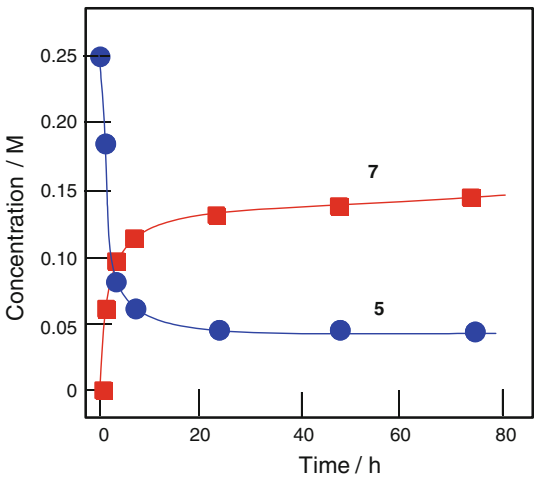
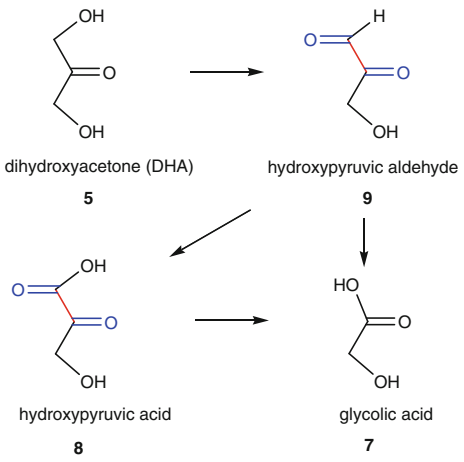


Fig. 9 Accumulation of glycolic acid (**7**) in the oxidation of dihydroxyacetone (**5**; initial concentration 0.25 M) with H_2O_2 (50% aqueous; initial concentration 0.75 M) catalyzed by complex **1a** (5×10^{-5} M) in the presence of oxalic acid (0.02 M) and added D_2O (0.2 mL). Solvent was acetonitrile, total volume of the reaction solution was 5 mL; 22 °C

oxidation with our '**1a**/carboxylic acid/H_2O_2/CH_3CN' system [72, 77]. This fact explains why in the glycerol oxidation we are able to obtain DHA in relatively high yield: when the concentration of glycerol is still high, the system oxidizes predominantly glycerol and not DHA. However, in the period of the reaction when the concentration of **4** is low and some hydrogen peroxide is still present in the solution, DHA is oxidized extensively. If the concentration of H_2O_2 after oxidation of all glycerol is very low, obviously, the first product **5** will be not further oxidized. In a special experiment (Fig. 9) in the absence of glycerol, DHA is apparently oxidized primarily to hydroxypyruvic aldehyde **9** and hydroxypyruvic acid **8** (Scheme 4). In both compounds vicinal carbonyl groups are present and this facilitates the decarbonylation to afford



Scheme 4 Pathways of dihydroxyacetone oxidation

glycolic acid **7**. Previously we found that catalyst **1a** initiates oxidative decarboxylation of cyclohexanecarbaldehyde with molecular oxygen [115] and the system **1a**/carboxylic acid/H_2O_2/CH_3CN transforms acetone to acetic acid [77]. The oxidation of DHA in the absence of glycerol afforded mainly glycolic acid. The yield of **7** after 72 h attained 60% based on starting DHA. Other products which were detected in the ^{1}H NMR spectrum as numerous very small signals were produced in total yield 24%. It is noteworthy, that due to complete consumption of hydrogen peroxide and some decomposition of **1a** no further substantial oxidation of glycolic acid (to oxalic acid, CO_2 etc.) after 10 h was noticed.

Figure 10 demonstrates the accumulation of main products in the process catalyzed by heterogenized catalyst **1b**. Yield of the products after 1 h does not depend on the amount of **1b** (Fig. 11) which is similar to the behavior found for the oxidation of 1-phenylethanol (compare with Fig. 7). One can assume that this independence is due to the aggregation of heterogeneous forms of the catalyst which leads to the contraction of the catalytically active surface.

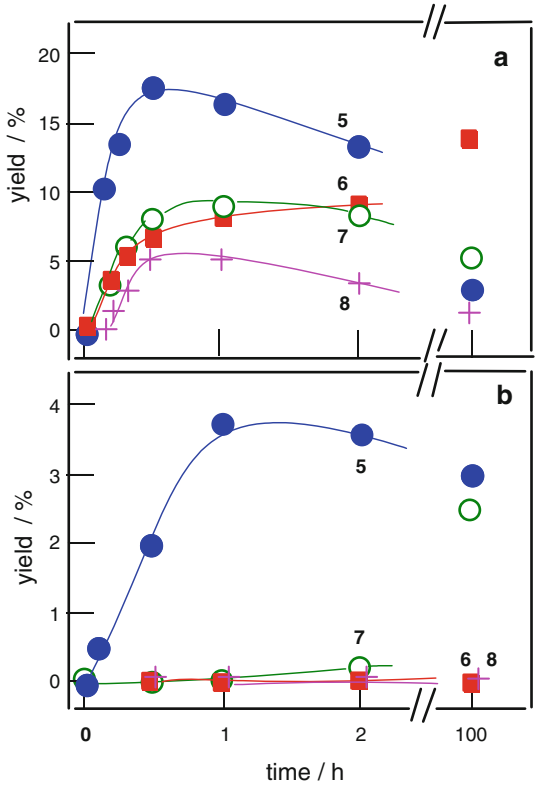


Fig. 10 Glycerol oxidation catalyzed by heterogenized complex **1b**. Kinetics of accumulation of the following products are shown: dihydroxyacetone (**5**), glyceric acid (**6**), glycolic acid (**7**), and hydroxypyruvic acid (**8**). Conditions: glycerol, 0.21 M; H_2O_2 (50% aqueous), 0.3 M; **1b**, 5 mg (which is equivalent to 4.4×10^{-4} M Mn ions); oxalic acid: 0.002 M (Graph *a*) and 0 M (Graph *b*). Solvent was acetonitrile, total volume of the reaction solution was 5 mL; 22 °C

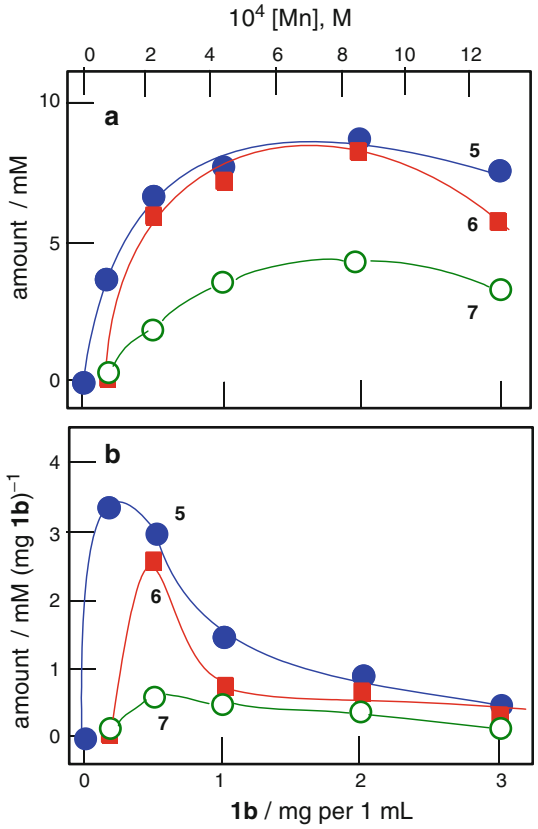


Fig. 11 Dependence of concentrations (Graph *a*: mM; Graph *b*: mM per 1 mg of **1b**; 1 mg/mL is equivalent to 4.4×10^{-4} M Mn ions) of dihydroxyacetone (**5**), glyceric acid (**6**), and glycolic acid (**7**) after 1 h in the oxidation of glycerol (0.21 M) with H_2O_2 (0.3 M; 50% aqueous) catalyzed by compound **1b** on initial amount of **1b** (expressed as mg per 1 mL of the solution and also as equivalent concentration of Mn ions). Solvent was acetonitrile; total volume of the reaction solution was 5 mL; 22 °C

In order to check if there is some leaching of the cation $[LMn(O)_3MnL]^{2+}$ from solid compound **1b** to the reaction solution, we carried out the following experiment. A mixture of **1b** (5 mg), H_2O_2 (50% aqueous; 0.1 mL; 0.3 M), oxalic acid (0.002 M) and acetonitrile (4.8 mL) was stirred at 22 °C for 1 h and then the solid catalyst was removed by centrifugation and consequent filtration. Glycerol (0.1 g) was added to the homogeneous solution and the reaction was continued at 22 °C for 1 h. After the standard work up procedure the amount of DHA was measured by ^{1}H NMR. This amount turned out to be only 0.9 mM (yield 0.4% based on initial glycerol). Other products were not detected. In the analogous experiment without removing catalyst **1b** the following products (% based on glycerol) were obtained after 1 h: DHA (16), glyceric acid (8), glycolic acid (8), hydroxypyruvic acid (2). These experiments indicate that the glycerol oxidation occurs predominantly on the surface of catalyst **1b**.

The experiments on recycling are shown in Fig. 12. After each run (the reactions were carried out only for the relatively low conversion of glycerol and in low yields of products) catalyst **1b** was separated using centrifugation and filtration, washed with acetonitrile and dried in air at room temperature during 24 h. It can be seen that some loss of activity upon catalyst recycling has been found only for the second run. The third and fourth runs gave the same yields of the products. Thus, the catalyst can be easily isolated from the reaction mixture and re-used many times without sufficient loss of activity. The enhanced stability of the immobilized catalyst is a remarkable fact. It may be due to the occurrence of the substrate oxidation on the solid surface [80]. Thus, TMTACN ligands of the catalyst (which

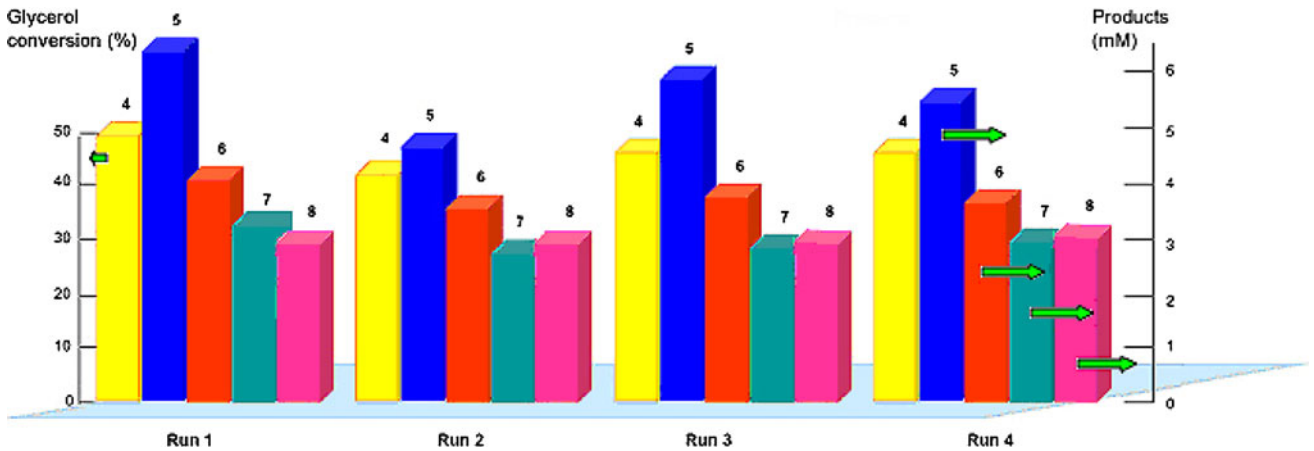


Fig. 12 Glycerol (**4**) conversion (%) and yield (% based on starting glycerol) of dihydroxyacetone (**5**), glyceric acid (**6**) glycolic acid (**7**), and hydroxypyruvic acid (**8**) after 1 h in the oxidation of glycerol (0.21 M) with H_2O_2 (0.3 M; 50% aqueous) catalyzed by compound **1b** (5 mg per 5 mL of the reaction solution, which is equivalent to 4.4×10^{-4} M Mn ions) in recycling experiments. Solvent was acetonitrile; 22 °C

can be relatively easily destroyed in the solution) are protected with the surrounding voluminous polyoxometalate species. Moreover, these species can take part in some redox processes which also protect the catalyst anion. A special study is, however, required.

3 Conclusions

This study demonstrates that both soluble **1a** and heterogenized **1b** catalysts can be successfully used for the efficient oxidation of 1-phenylethanol and glycerol by hydrogen peroxide. In the 1-phenylethanol oxidation catalyzed by **1a** turnover number (moles of acetophenone formed per one mole of catalyst **1a**) attained 15,000 after 3 h, and the yield of acetophenone was 94%. Turnover frequency in the initial period was 7,400 h^{-1}. The oxidation of glycerol catalyzed by **1a** represents one of the first examples of metal-catalyzed glycerol oxidation by a *homogeneous* system [116]. The yield of valuable products attained 45%. The oxidation on **1b** represents the first example of the glycerol transformation catalyzed by a *heterogenized* metal complex. The advantage of our method is that the oxidations were carried out at ambient temperature, and due to this in the case of large-scale process over-heating and the possibility of explosions in large reactors are significantly reduced.

4 Experimental

Catalyst **1b** was prepared as described by Veghini, Fischer and coworkers [98]. The reactions of oxidation of 1-phenylethanol and glycerol were carried out in acetonitrile in air in thermostated Pyrex cylindrical vessels with vigorous stirring. Catalyst **1a** and oxalic acid were used in the form of stock solutions. Catalyst **1** was introduced into the reaction mixture and the substrate (1-phenylethanol or glycerol) was then added. The reaction started when hydrogen peroxide (50% in H_2O) was introduced in one portion. Typically the total volume of the reaction solution was 5 mL. Concentrations of products obtained in the oxidation of alcohols after certain time intervals were measured using ^1H NMR method (acetone-d_6 was added to the samples; "Bruker AV-300" instrument, 300 MHz). For the determination of concentrations of substrates and products, corresponding signals were integrated using added 1,4-dinitrobenzene as a standard. The initial accumulation rate W_0 was measured from the slope of tangent of the kinetic curve in the initial period of the reaction.

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