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Mild homogeneous oxidation of alkanes and alcohols including glycerol with *tert*-butyl hydroperoxide catalyzed by a tetracopper(II) complex

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ABSTRACT

The homogeneous catalytic system composed of the aqua-soluble tetracopper(II) triethanolaminate complex $[O \subset Cu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$ (**1**), *t*-BuOOH (TBHP), water and acetonitrile solvent (optional) has been applied for the mild oxidation of (i) linear and cyclic alkanes to the corresponding alkyl peroxides, alcohols and ketones, (ii) secondary or primary alcohols to ketones or aldehydes, respectively and (iii) glycerol (GLY) to dihydroxyacetone (DHA). Unusual regio-, bond and stereoselectivity parameters have been determined for the alkane oxygenations and discussed in terms of possible steric, hydrophobic and electronic effects. In alcohol oxidations, secondary alcohols are the most reactive substrates. Yields and TONs up to 82% and 1200, respectively, have been obtained in the oxidation of isopropanol to acetone. The selective oxidation of GLY to DHA by the **1**/TBHP system has been also achieved, although providing lower conversions. The **1**/H_2O_2 system for the GLY oxidation is particularly advantageous in terms of selectivity and oxidant efficiency. These systems constitute one of the first examples of a metal-catalyzed oxidation of glycerol under *homogeneous* conditions.

1. Introduction

The development of new methods for the selective oxidative functionalization of C–H bonds in various organic molecules continues to be a challenging topic in areas of organic chemistry and catalysis [1–10]. The atom-efficient and mild oxidations of alkanes into a mixture of alkyl hydroperoxides, alcohols and ketones [3–10] and, in turn, further transformations of alcohols to ketones and aldehydes [11–16] concern particularly interesting reactions of high significance, because they lead to the production of added value chemicals. Moreover, alkanes are known as the most abundant and relatively cheap carbon raw materials, but very inert for efficient transformations under mild conditions [3–10], while the selective oxidations of alcohols are often limited by the use of stoichiometric metal-containing oxidants (e.g. $KMnO_4$, CrO_3) [11–16].

In pursuit of our general interest in the development of new selective routes and catalytic systems for the oxidative functionalization of alkanes and other substrates [3–6,17–34], some of us have designed a series of multicopper(II) catalysts [35–45]. Among them, the hydrosoluble tetracopper(II) triethanolaminate complex $[O \subset Cu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$ (**1**) (Scheme 1) is the most active and versatile Cu catalyst for (i) the oxygenation of alkanes by hydrogen peroxide [40–42], (ii) the hydrocarboxylation of alkanes with CO and H_2O to carboxylic acids [43,44] and (iii) the aerobic oxidation of benzylic alcohols to aldehydes [45]. The high activity and versatility of complex **1** can be associated with its multicopper N,O-cluster structure, which somehow mimics the catalytic function of particulate methane monooxygenase (pMMO), a unique copper enzyme capable of catalyzing the oxidation of various substrates including alkanes [46–48].

Bearing these features in mind, the main objective of the present work consists in broadening the scope of catalytic transformations with **1** to other alkanes, aliphatic alcohols and glycerol (GLY), using a different oxidizing agent, *tert*-butyl hydroperoxide (TBHP). As alkanes, we have chosen *n*-heptane, *n*-octane, cyclohexane, methylcyclohexane (MCH) and stereoisomeric 1,2-dimethylcyclohexanes (*cis*- and *trans*-DMCH), aiming at studying the effect of organic oxidant on the regio-, bond and stereoselectivity parameters, and the overall efficiency of such a catalytic system.

Besides, the search for the selective oxidation of glycerol constitutes an important goal, since nowadays this alcohol is an abundant bio-renewable feedstock from the biodiesel

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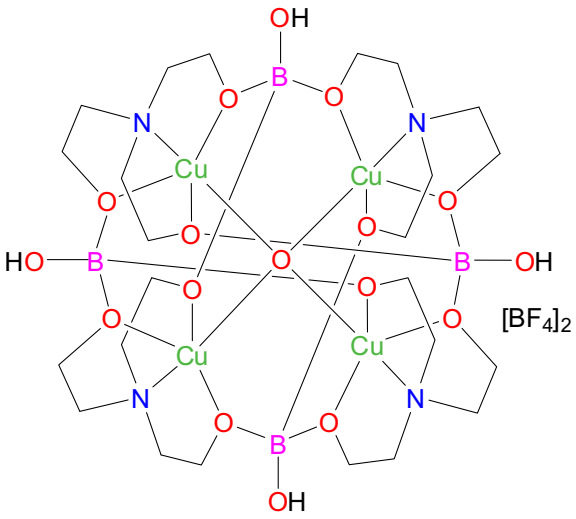
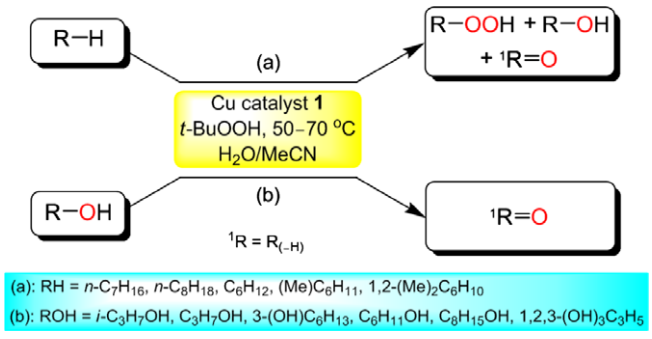


Scheme 1. Molecular formula of copper catalyst **1**.

manufacture, suitable for the production of a wide variety of organic intermediates and high-end chemicals [49–55]. However, the clean and selective transformations of glycerol are particularly difficult to realize due to the (i) competing reactivity of all the three carbon atoms of the molecule, (ii) facile subsequent oxidation of the primary formed products and (iii) easy oxidative degradation of GLY itself to give products of deep oxidation: formaldehyde, formic acid and carbon dioxide [49–55]. Although some interesting *heterogeneous* catalytic systems (typically based on supported metallic Au, Pd or Pt catalysts) for the oxidation of glycerol have been recently developed [56–60], the *homogeneous* oxidation of glycerol by peroxides remains almost unstudied. This contrasts with the significant body of research [11–16] on the homogeneous oxidations of simple primary or secondary alcohols. To this regard, in the present work, along with glycerol, we have also used isopropanol and propanol as its simple models in the Cu-catalyzed oxidations by TBHP.

Here, we report on the application of the homogeneous catalytic system (Scheme 2) composed of complex **1**, TBHP, water and acetonitrile (optional) for the mild oxidation of (i) linear and cyclic alkanes to the corresponding alkyl peroxides, alcohols and ketones, (ii) secondary or primary alcohols to ketones or aldehydes and (iii) glycerol to dihydroxyacetone. To our knowledge, the latter transformation constitutes one of the first examples of the *homogeneous* metal-catalyzed oxidation of glycerol.



Scheme 2. Oxidation of alkanes (a) and alcohols (b) by the **1**/TBHP system (propionic acid is also formed in the oxidation of C_3H_7OH).

2. Experimental

2.1. Materials and methods

All chemicals were obtained from commercial sources and used as received. Catalyst **1** was prepared according to the previously described procedure [40]. GC analyses were performed on an Agilent 6890 series gas chromatograph (N_2 was a carrier gas, FID) with a capillary column (30 m × 0.25 mm × 0.25 μm, BP-20, SGE). Attribution of peaks was made by comparison with chromatograms of authentic samples and, in some cases, by GC–MS analyses using a Shimadzu QP-2010 Plus instrument (He as the carrier gas), equipped with a capillary column (BP-20, SGE). Nitromethane was used as GC internal standard.

2.2. Oxidation of alkanes and alcohols

The oxidation reactions of alkanes and alcohols were typically carried out in air in thermostated Pyrex cylindrical vessels or round-bottom flasks with vigorous stirring and using MeCN as solvent. **CAUTION**: the combination of air or molecular oxygen and a peroxide (TBHP or H_2O_2) with organic compounds at elevated temperatures may be explosive! In a typical experiment, catalyst **1** was introduced into the reaction mixture in the form of a stock solution in water. The substrate (alkane or alcohol) was then added, and the reaction started when TBHP (70% in H_2O) or hydrogen peroxide (50% in H_2O) was introduced in one portion. The reactions were stopped by cooling and analyzed by GC. Blank tests indicate that only traces of products can be formed in the absence of the copper catalyst.

Since the oxygenation of alkanes usually gives rise to the formation of the corresponding alkyl peroxides as the main primary products, their quantification was performed by a simple method developed earlier by some of us [6,17,18,61]. In accordance with this method, the comparison of the chromatograms of the reaction samples before and after reduction with PPh_3 allows us to estimate real concentrations of the three primary products (alkyl peroxide, alcohol and ketone). For precise determination of oxygenate concentrations, only the data obtained after reduction of the reaction sample with PPh_3 were usually used, taking into account that the original reaction mixture typically contained the three above-mentioned products.

2.3. Oxidation of glycerol

The oxidation reactions were performed in air in thermostated round-bottom flasks or Pyrex cylindrical vessels. In a typical experiment, catalyst **1** (5.0 μmol; 150 μL of a 0.033 M solution in H_2O) was mixed with glycerol (1.0–2.5 mmol used as a 5 M solution in H_2O), water (0.25–1.30 mL) and acetonitrile (2.8–3.8 mL; to reach the 5.0 mL total volume of the reaction mixture), followed by the addition of oxidant, TBHP (70% in H_2O) or H_2O_2 (35% in H_2O). The resulting mixture was vigorously stirred for 0.5–30 h at 25–70 °C, and then 50 μL of $MeNO_2$ (as GC internal standard) was added. An aliquot (0.5 mL) of the obtained solution was diluted with MeOH (ca. 5–10 volumes) and analyzed by GC. For the oxidations in the presence of base, prior neutralization of an aliquot with aqueous HCl was undertaken.

Additional experiments were performed in the presence of HCl, Na_2CO_3 or TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), which were added before the oxidant in separate batches. Blank tests confirmed that the oxidation of glycerol does not proceed in the absence of the copper catalyst.

3. Results and discussion

3.1. Oxygenation of alkanes: selectivity features

The investigation into alkane oxidations has been undertaken by reacting, at 50 °C in MeCN medium, an alkane with TBHP (70% in H_2O) in the presence of compound **1**. Previously, we have found [40–42] that the efficiency of catalyst **1** when using the H_2O_2 oxidant can be dramatically improved in the presence of an acid promoter. However, no positive influence of an acid additive is detected for the **1**/TBHP system studied in the present work. This can suggest the involvement of different mechanistic pathways that depend on the type of oxidant (H_2O_2 vs. TBHP) used for alkane oxidations with catalyst **1**. To prove this possibility and shed some light on the active intermediate species, we have now studied the product distribution patterns and regio-, bond and stereoselectivity parameters in the alkane oxidations with the **1**/TBHP system (Scheme 2, reaction a). Cyclohexane, *n*-heptane, *n*-octane, methylcyclohexane (MCH), *cis*- and *trans*-1,2-dimethylcyclohexane (*cis*- and *trans*-DMCH) have been used as substrates. The obtained results are shown in Fig. 1 and Tables 1–3.

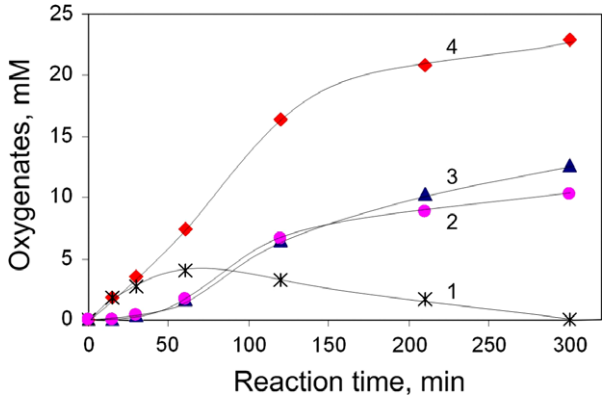


Fig. 1. Accumulation of oxygenates: cyclohexyl peroxide CyOOR (curve 1), cyclohexanol (curve 2), cyclohexanone (curve 3) and total (curve 4) along the time in the oxidation of cyclohexane by the **1**/TBHP system. Reaction conditions: $[\mathbf{1}]_0$ = 1.0 mM, $[H_2O]_{total}$ = 3.1 M, $[TBHP]_0$ = 0.92 M (70% in H_2O), $[cyclohexane]_0$ = 0.46 M, MeCN up to 5 mL total volume, 50 °C.

The character of the kinetic curves for the accumulation of oxygenates in the oxidation of cyclohexane (Fig. 1) indicates that cyclohexyl peroxides (CyOOR, R = H and/or *t*-Bu) are formed as primary products. Their concentration (curve 1), after reaching the maximum at 60 min of reaction time, starts to decrease due to the gradual decomposition to give the final products, cyclohexanol (curve 2) and cyclohexanone (curve 3). The overall process of cyclohexane oxidation (curve 4) is rather fast in the 0–150 min of time interval, followed by deceleration beyond this time. It is interesting that cyclohexyl peroxides are not detected after 300 min of the reaction, while the concentrations of cyclohexanol and cyclohexanone are comparable (alcohol/ketone molar ratio, *A*/*K*, is ca. 0.9). It is necessary to emphasize that, in the general case, the *A*/*K* ratio determined after reduction of the reaction sample with PPh_3 corresponds to the real (cyclohexyl peroxides + *A*)/*K* ratio in the reaction solution.

The product distribution pattern is changed in the course of *n*-heptane and *n*-octane oxidations by the **1**/TBHP system (Table 1; see also Fig. S1 for formulae of oxygenate isomers and a typical chromatogram). After the reduction of peroxides with PPh_3, the secondary alcohols are the main products at the beginning of the reaction (30 min). However, their concentrations drop on prolonging the reaction time to 60 min due to further oxidation of the alcohols to the corresponding ketones. Beyond this time, the concentrations of alcohols slightly decrease, while those of ketones have an increasing trend, resulting in diminution of the alcohol/ketone (*A*/*K*) molar ratios. One of the most remarkable features of the reaction under consideration is the finding that the C(2) atom of the *n*-heptane and *n*-octane chain is the most reactive. This is reflected by the regioselectivity parameters C(1):C(2):C(3):C(4) of 1:34:23:21 and 1:65:32:30 for *n*-heptane and *n*-octane, respectively (Table 1). These values are significantly higher than those of 1:8:7:5 and 1:7:6:5 previously observed [42] for the oxidation of *n*-heptane by the **1**/CF_3COOH/H_2O_2 and $Cu(NO_3)_2/HNO_3/H_2O_2$ systems, respectively (Table 3, entries 1–3), thus suggesting the possible involvement of different types of active oxidizing species. Besides, the C(2) position is a preferable oxidation site in the biological hydroxylation of alkanes catalyzed by pMMO [47,48].

Table 1
Accumulation of oxygenates in the oxidation of *n*-heptane and *n*-octane with TBHP catalyzed by complex **1**.[a]

Time (min)	Products (relative concentrations)[b]							C(1):C(2):C(3):C(4)[c]	*A*/*K*[d]
	ol-4	**ol-3**	**ol-2**	**ol-1**	**one-4**	**one-3**	**one-2**		
Oxidation of n-heptane									
30	7	15	23	1.0	0	0	0	1:34:23:21	≫1
60	4	7	13	1.0	4	8	10	1:20:10:13	1.10
120	4	5	9	1.0	7	15	19	1:14:8:13	0.48
180	5	6	10	1.0	9	19	25	1:15:9:14	0.40
240	5	7	10	1.0	10	21	27	1:15:10:15	0.39
300	6	7	11	1.0	13	28	37	1:17:11:18	0.33
Oxidation of n-octane									
30	20	21	43	1.0	26	29	35	1:65:32:30	0.92
60	12	13	22	1.0	28	31	39	1:32:19:18	0.48
90	5	5	10	1.0	14	16	20	1:15:8:8	0.42
120	4	4	8	1.0	10	13	16	1:12:7:7	0.44
180	4	4	6	1.0	11	13	16	1:10:6:6	0.37

[a] Reaction conditions: $[\mathbf{1}]_0$ = 1.0 mM, $[H_2O]_{total}$ = 2.1 M, $[TBHP]_0$ = 0.46 M (70% in H_2O), $[alkane]_0$ = 0.46 M, MeCN up to 5 mL total volume, 50 °C. Abbreviations of products **ol** and one refer to the corresponding alcohols (e.g. heptanol-1) and ketones (e.g. heptanone-2) derived from *n*-heptane or *n*-octane, respectively. Typical chromatogram of the reaction mixture in the oxidation of *n*-heptane is shown in Supplementary material (Fig. S1).

[b] Concentrations of isomers (after reduction with PPh_3) are given relative to the concentration of **ol-1** ($[\mathbf{ol\text{-}1}]$ = 1.0).

[c] Regioselectivity parameters C(1):C(2):C(3):C(4) are relative normalized reactivities of hydrogen atoms at carbon atoms C(1), C(2), C(3) and C(4) of alkane chain, determined on the basis of concentrations of alcohol isomers after reduction with PPh_3.

[d] The *A*/*K* ratio corresponds to the alcohol/ketone molar ratio, i.e. total concentration of all the alcohol isomers divided by total concentration of all the ketone isomers determined after reduction with PPh_3.

Table 2
Oxidation of methylcyclohexane (MCH) with TBHP catalyzed by complex **1**.[a]

Time (min)	Oxygenate products[b] (mM)												*A*/*K*[c]	(**P6** + **P7**):(**P8** + **P10**):(**P9** + **P11**)[d]	1°:2°:3°[e]
	P1	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**	**P11**	**P12**			
30	0.34	0.47	4.72	1.92	0.70	0.17	0.33	0.16	0.60	0.24	0.97	0.11	3.1	1:8:3	1:16:128
60	0.44	1.48	5.48	2.78	1.02	0.25	0.39	0.19	0.70	0.30	1.17	0.14	2.2	1:8:3	1:15:121
140	0.54	1.85	6.56	3.85	1.41	0.25	0.43	0.22	0.76	0.34	1.37	0.16	2.0	1:8:3	1:16:123
200	0.60	2.07	7.00	4.54	1.68	0.22	0.50	0.25	0.81	0.37	1.45	0.15	1.8	1:9:3	1:17:138
260	0.65	2.34	6.87	5.27	1.95	0.19	0.50	0.25	0.79	0.39	1.49	0.17	1.6	1:9:3	1:17:123
380	0.64	2.88	6.49	6.89	2.55	0.19	0.53	0.25	0.79	0.42	1.62	0.19	1.2	1:9:3	1:13:100

[a] Reaction conditions: $[\mathbf{1}]_0$ = 1.0 mM, [total H_2O]$_0$ = 3.1 M, $[TBHP]_0$ = 0.46 M (0.33 mL; 70% in H_2O); $[MCH]_0$ = 0.46 M (0.29 mL); MeCN up to 5 mL total volume; 50 °C.
[b] Concentrations of oxygenates based on GC analysis after reduction with PPh_3. Oxygenate products: **P1**: cyclohexanecarboxaldehyde, **P2**: 2-methylcyclohexanone, **P3**: 1-methylcyclohexanol, **P4**: 3-methylcyclohexanone, **P5**: 4-methylcyclohexanone, **P6**: *trans*-2-methylcyclohexanol, **P7**: *cis*-2-methylcyclohexanol, **P8**: *trans*-3-methylcyclohexanol, **P9**: *trans*-4-methylcyclohexanol, **P10**: *cis*-3-methylcyclohexanol, **P11**: *cis*-4-methylcyclohexanol, **P12**: cyclohexylmethanol. Molecular formulae of oxygenate products **P1**–**P12** are given in Supplementary material (Fig. S2a). Typical chromatogram of the reaction mixture is shown in Fig. S2b.
[c] The *A*/*K* ratio corresponds to the alcohol/ketone molar ratio, i.e. total concentration of all the alcohol isomers divided by total concentration of all the ketone isomers.
[d] Molar ratios between methylcyclohexanols in positions of the methyl group 2 (products **P6** and **P7**), 3 (products **P8** and **P10**) and 4 (products **P9** and **P11**).
[e] Bond selectivity, i.e. relative normalized reactivities of hydrogen atoms at primary (1°), secondary (2°) and tertiary (3°) carbon atoms of MCH.

Table 3
Comparative representation of selectivity parameters in the oxidation of alkanes in acetonitrile by different systems.

Entry	System	C(1):C(2):C(3):C(4)		1°:2°:3°	*Trans*/*cis*	
		n-Heptane	*n*-Octane	MCH	*Cis*-DMCH	*Trans*-DMCH
1	**1**/TBHP (50 °C)[a]	1:34:23:21	1:65:32:30	1:16:128	0.4	0.1
2	**1**/CF_3COOH/H_2O_2 (50 °C)[b]	1:8:7:5	1:5:5:4	1:5:14	0.8	0.8
3	$Cu(NO_3)_2$/HNO_3/H_2O_2 (50 °C)[b]	1:7:6:5	0.9	0.7		
4	**Mn$_2$**/$(COOH)_2$/TBHP (50 °C)[c]	1:14:13:12	1:17:12:11	1:0.3:0.6	0.2	7.3
5	**Mn$_2$**/$MeCO_2H$/H_2O_2 (25 °C)[c]	1:46:35:34	1:29:25:24	1:26:200	0.3	4.1
6	$NaAuCl_4$/H_2O_2 (75 °C)[d]	1:35:25:23	1:116:255			

[a] Reaction conditions for entry 1 are similar to those of Tables 1 and 2 (for linear alkanes), and Fig. 1 (for cycloalkanes). All parameters were measured after reduction of the reaction mixtures with PPh_3 before GC analysis and calculated based on the ratios of isomeric alcohols. Parameters C(1):C(2):C(3):C(4) are relative normalized reactivities of H atoms at carbon atoms C(1), C(2), C(3) and C(4) of *n*-heptane or *n*-octane chain. Parameters 1°:2°:3° are relative normalized (taking into account the number of H atoms at each carbon atom) reactivities of hydrogen atoms at primary, secondary and tertiary carbon atoms of branched alkanes. Parameter *trans*/*cis* is determined as the ratio of the formed tertiary alcohol isomers with mutual *trans* and *cis* orientation of the methyl groups.
[b] For this system, see [42].
[c] Compound **Mn$_2$** is the complex $[Mn_2L_2(O)_3]^{2+}$, where L is 1,4,7-trimethyl-1,4,7-triazacyclononane; for this system, see [62,64–66].
[d] For this system, see [67].

Fig. 2 demonstrates the regioselectivity profiles for the oxidation of *n*-heptane and *n*-octane by certain systems [25,32,42,62,63]. It can be seen that the regioselectivity parameters for the oxidation with TBHP catalyzed by **1** (profile *a*) are very close to those found previously [32] in the reaction with a dinuclear manganese complex containing a strongly hindered reaction center (profile *b*). This catalyst is believed to operate without the participation of free hydroxyl radicals. An analogous dimanganese complex that contains a less hindered reaction center exhibits a noticeably lower regioselectivity with respect to the C(2) position of the alkane chain as well as with respect to the methyl group (profile *c*). A "simple" Cu(I) complex catalyzes the oxidation of linear alkanes with a comparable regioselectivity (profile *d*). This catalytic system apparently involves *tert*-butoxy radicals as oxidizing species [63]. Profiles *e* and *f* correspond to the oxidations by the **1**/H_2O_2/CF_3COOH and $Os_3(CO)_{12}$/H_2O_2/py systems, respectively. They exhibit very low selectivities due to the oxidation with participation of hydroxyl radicals. A comparison of the profile *a* with profiles *e* and *f* clearly demonstrates that the oxidation by the **1**/TBHP system does not involve free hydroxyl radicals.

The oxidation of methylcyclohexane (MCH) is a particularly interesting reaction to study the selectivity features due to the variety of differently hindered C–H bonds in this molecule (Table 2). The oxidation of this cycloalkane proceeds faster than those of linear alkanes, what can be explained by its cyclic character and the presence of the more reactive tertiary carbon atom. Hence, the corresponding ketones **P2**, **P4** and **P5**, and aldehyde **P1** (hereinafter all product numbers **P1**–**P12** are those of Table 2; see Fig. S2a for the formulae of the isomeric products) are detected in appreciable amounts already after 30 min reaction time. Their concentrations steadily increase on extending the reaction time to 380 min, whereas the alcohol products are typically not accumulated due to their further oxidation (except from alcohols **P3** and **P11**). Such a trend can be monitored by the decrease in the *A*/*K* molar ratio from 3.1 to 1.2 on rising the reaction time from 30 to 380 min, respectively. Although the oxygenation of MCH at the tertiary carbon atom with formation of 1-methylcyclohexanol (**P3**) as the main product has been expected, an interesting reactivity of the secondary carbon atoms was revealed. In particular, the position 2 relatively to the methyl group of the substrate is about nine and three times less reactive than the corresponding positions 3 and 4, respectively, regarding the formation of alcohol products [Table 2, parameter (**P6** + **P7**):(**P8** + **P10**):(**P9** + **P11**)]. This observation indicates the noticeable sterical hindrance that is apparently due to the involvement of a bulky oxidizing species. In fact, the bond selectivity parameter 1°:2°:3° of 1:16:128 (Table 2) differs significantly from the respective values observed for the systems where HO$^{\cdot}$ (compare also Fig. S2b and S2c) or *t*-BuO$^{\cdot}$ [3–6,62,64,65] is active species in the oxidation of methylcyclohexane (Table 3, entries 2–4). Comparable parameters of bond selectivity 1°:2°:3° have been reported for the systems based on Mn [62,64–66] (1:26:200) and Au [67] (1:116:255) compounds (Table 3).

It is noteworthy that the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexanes (DMCH) by the **1**/TBHP system (Table 3, entry 1)

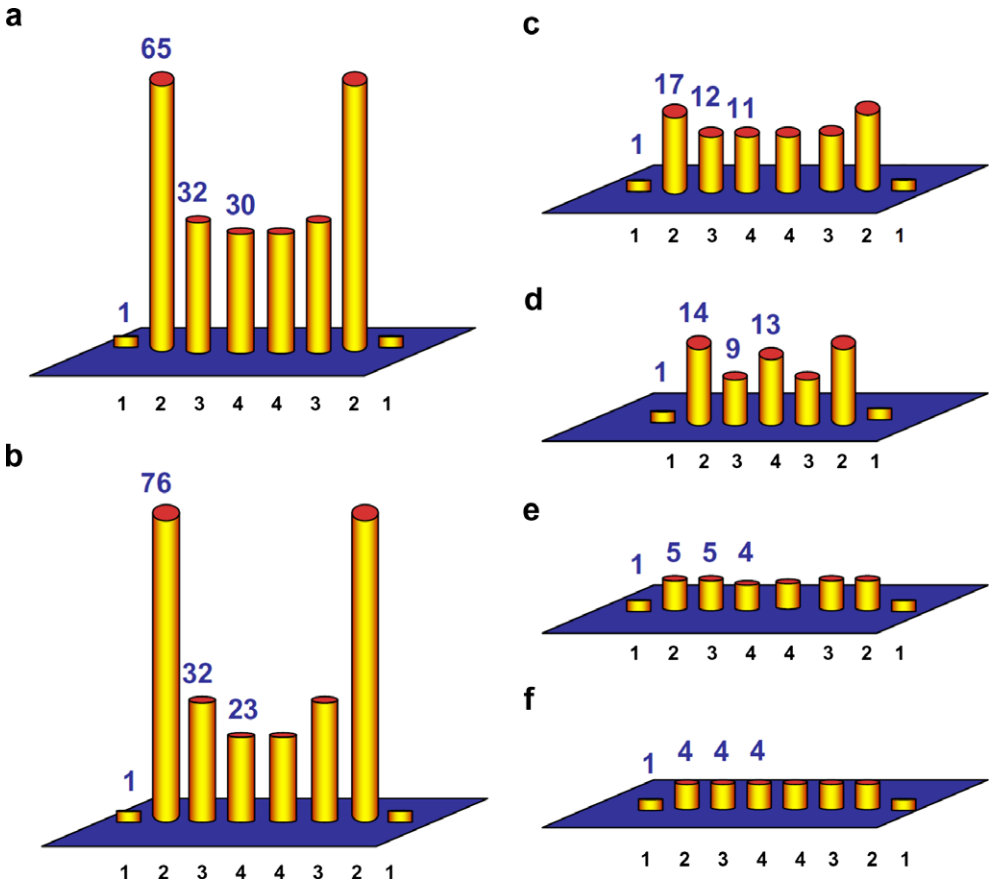


Fig. 2. The regioselectivity profiles [bars correspond to the normalized reactivities of methylene protons in positions C(2), C(3) and C(4) of the alkane chain relative to the reactivity (defined as a unity) of methyl protons in position C(1)] for the oxidation of *n*-octane in acetonitrile by the systems: **1**/TBHP (a) (this work), complex $[Mn_2(R\text{-}LMe^{2R})_2(\mu\text{-}O)_2]^{3+}(PF_6)_3$ (where LMe^{2R} is 1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane)/oxalic acid/TBHP (b) [32], complex $[Mn_2(LMe_3)_2(\mu\text{-}O)_3]^{3+}(PF_6)_2$ (where LMe_3 is 1,4,7-trimethyl-1,4,7-triazacyclononane)/oxalic acid/TBHP (c) [62], $Cu(NCMe)_4BF_4$/TBHP (*n*-heptane was used as a substrate) (d) [63], **1**/H_2O_2/CF_3COOH (e) [42], and $Os_3(CO)_{12}/H_2O_2$/py (f) [25].

proceeds with a substantial inversion of configuration, as attested by the respective *trans*/*cis* product molar ratios of 0.4 and 0.1. These values are essentially different from those (ca. 0.7–1.0) typical for the reactions involving HO· radicals (Table 3, entries 2 and 3). Besides, the *trans*/*cis* value obtained in the oxidation of *cis*-DMCH is comparable to those (ca. 0.2–0.3) observed in the oxidations with a dimanganese complex [62,64–66] (entries 4 and 5) which, in contrast to the **1**/TBHP system (*trans*/*cis* = 0.1), do not lead to inversion of the configuration when oxidizing *trans*-DMCH, as shown by the very high *trans*/*cis* values in the 4.1–7.3 range.

Based on the literature background [42,62,64–67] and all the above-mentioned features regarding product distribution patterns and selectivity parameters in alkane oxygenations, we can conclude that the oxidation by the **1**/TBHP system occurs with the participation of a sterically hindered reaction center. Although the mechanistic details are uncertain, based on the related literature data [42,48,62,64–67], we assume that the present alkane transformations can possibly proceed in a hydrophobic pocket with the potential involvement of active oxo/peroxo copper species, as well as with the participation of a bulky oxidizing species generated from TBHP. In this regard, some mechanistic steps on the formation of a peroxo copper derivative were previously proposed by us for the related **1**/H_2O_2 system on the basis of ESR, UV–vis, kinetic and selectivity methods [42]. Besides, in spite of possessing a very distinct structure from that of the present catalyst, the hydrophobic cavity of the tricopper active site of pMMO has been recently proven [48] to be responsible for the unusual selectivities observed in the oxidations of alkanes and olefins. Moreover, different peroxo derivatives of copper are intermediates in various biological [68,69] and chemical transformations [42,70,71]. Alternatively, the radical *t*-BuO· formed from TBHP and a copper ion in a narrow hydrophobic environment can abstract with a high selectivity hydrogen atom from C–H bonds of the hydrocarbon. Enhanced regioselectivity is known for biological oxidizing systems (e.g., pMMO [47,48], cytochrome P450 [72]) and for reactions *in vitro* that occur in narrow cavities and channels of microporous materials [29,73,74].

It should be noted in the end of this section that we have shown that in the course of alkane oxygenations by the **1**/TBHP system occurring with unusual regioselectivity, the obtained alcohol products also undergo further oxidation to the corresponding ketones. The investigation into the latter reaction with regard to different alcohol substrates is discussed below.

3.2. Oxidation of isopropanol, propanol and other alcohols

Aiming at evaluating the relative reactivity of primary and secondary alcohols toward the oxidation by the **1**/TBHP system (Scheme 2, reaction b), we have used isopropanol and propanol as simple substrate models related to glycerol. In addition, some other alcohols have also been tested. The obtained results are summarized in Tables 4 and 5, and Figs. 3–5.

Isopropanol, in contrast to alkanes, is more reactive and can be oxidized by the **1**/TBHP system even at 25 °C, leading to ca. 26%

Table 4
Oxidation of isopropanol to acetone catalyzed by complex **1**.[a]

Entry	$[Me_2CHOH]_0$ (M)	Oxidant	T (°C)	Time (h)	Yield of acetone[b] (%)
1	1.0	TBHP	25	5	25.6
2	1.0	TBHP	50	3	38.0
3	0.5	TBHP	50	3	58.0
4	0.5	TBHP	70	3	81.6
5[c]	1.0	TBHP	50	3	35.0
6	1.0	H_2O_2	25	5	1.0

[a] Reaction conditions (unless stated otherwise): $[\mathbf{1}]_0$ = 1.0 mM, $[oxidant]_0$ = 2 M [TBHP (70% in H_2O) or H_2O_2 (35% in H_2O)], MeCN up to 5 mL total volume.
[b] Molar yield (%) [moles of acetone/100 mol of isopropanol] determined by GC analysis.
[c] In the presence of CF_3COOH (10^{-2} M).

Table 5
Oxidation of secondary and primary alcohols by the **1**/TBHP system[a].

Entry	Alcohol	$[TBHP]_0$ (M)	T (°C)	Time (h)	Product yield[b] (%)
1	Propanol	2.0	70	3	22.0
2	Isopropanol	2.0	70	3	81.6
3	Hexanol-1	1.0	50	3	2.0
4	Hexanol-1	2.0	70	3	2.7
5	Hexanol-3	1.0	50	3	11.4
6	Hexanol-3	2.0	70	3	48.4
7	Hexanol-3	2.0	70	6	58.3
8	Cyclohexanol	1.0	50	1	12.3
9	Cyclohexanol	1.0	50	3	17.4
10	Cyclooctanol	1.0	50	0.5	7.0
11	Cyclooctanol	1.0	50	1	15.9
12	Cyclooctanol	1.0	50	3	25.0
13	Cyclooctanol	2.0	70	3	47.6

[a] Reaction conditions: $[\mathbf{1}]_0$ = 1.0 mM, $[alcohol]_0$ = 0.5 M, TBHP (70% in H_2O), MeCN up to 5 mL total volume.
[b] Products refer to ketones or aldehydes and carboxylic acids when oxidizing secondary or primary alcohols, respectively. Molar yield (%) [moles of products/100 mol of alcohol] determined by GC analysis.

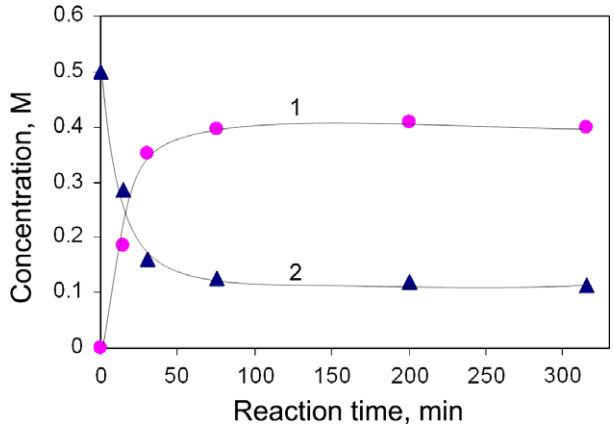


Fig. 3. Oxidation of isopropanol (curve 1) to acetone (curve 2) by the **1**/TBHP system. Reaction conditions: $[\mathbf{1}]_0$ = 1.0 mM, $[H_2O]_{total}$ = 4.2 M, $[TBHP]_0$ = 2.0 M (70% in H_2O), $[isopropanol]_0$ = 0.5 M, MeCN up to 5 mL total volume, 70 °C.

yield of acetone after 5 h (Table 4, entry 1). A slight increase in temperature to 50 °C accelerates the reaction, and a higher acetone yield (38%) is attained after 3-h reaction time (entry 2). The use of a fourfold excess of TBHP over isopropanol results in further yield growth to 58% (entry 3), while the augmentation of temperature from 50 to 70 °C leads to the maximum yield of 82% (entry 4). As can be seen from Fig. 3, the oxidation of isopropanol at 70 °C is rather fast and proceeds without auto-acceleration, reaching the

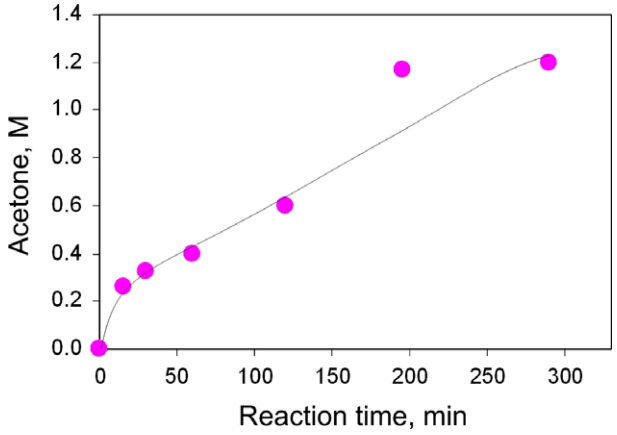


Fig. 4. Oxidation of isopropanol to acetone by the **1**/TBHP system in the absence of MeCN solvent. Reaction conditions: $[\mathbf{1}]_0$ = 1.0 mM, $[H_2O]_{total}$ = 4.2 M, $[TBHP]_0$ = 2.0 M (70% in H_2O), isopropanol up to 5 mL total volume, 60 °C.

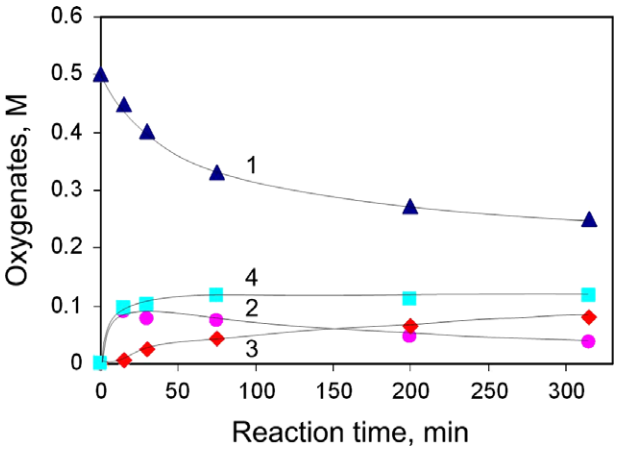


Fig. 5. Oxidation of propanol (curve 1) to propanal (curve 2) and propionic acid (curve 3) by the **1**/TBHP system (curve 4 corresponds to total of the products). Reaction conditions: $[\mathbf{1}]_0$ = 1.0 mM, $[H_2O]_{total}$ = 4.2 M, $[TBHP]_0$ = 2.0 M (70% in H_2O), $[propanol]_0$ = 0.5 M, MeCN up to 5 mL total volume, 70 °C.

plateau after 75-min reaction time. Comparison of the kinetic curves 1 and 2 (Fig. 3) supports the very high selectivity (close to 100%) to acetone even at a prolonged reaction time, thus pointing out the no occurrence of the over-oxidation of the isopropanol substrate and/or acetone product. The oxidation of isopropanol also proceeds quite efficiently in the absence of acetonitrile (Fig. 4), where isopropanol acts as both reagent and solvent. Under these reaction conditions, catalyst turnover numbers up to ca. 1200 can be obtained (Fig. 4).

As in the case of alkanes, the addition of an acid promoter (CF_3COOH) does not have a positive effect on the oxidation of isopropanol by the **1**/TBHP system (Table 4, entry 5 vs. 4). In contrast to TBHP, hydrogen peroxide is not a suitable reagent for alcohol oxidations, as attested by the rather low 1% yield of acetone after 5 h of reaction at 25 °C (Table 4, entry 6).

As expected for a primary alcohol, propanol is less reactive toward oxidation by the **1**/TBHP system (Table 5, entry 1), leading to maximum 22% overall yield of oxygenates (propanal and propionic acid). The kinetic curves for the accumulation of products in propanol oxidation (Fig. 5) are characteristic for a two-stage process. It consists of the formation of propanal as a primary product (curve 2), which is further oxidized to propionic acid (curve 3).

Although the total concentration of these two products is almost constant after 75-min reaction time, one should mention that the concentration of propanol continues to decrease (curve 1), thus pointing out the occurrence of its over-oxidation.

Another primary alcohol, hexanol-1, is much less reactive than propanol, leading to only 3% overall yield of hexanal and hexanoic acid (Table 5, entry 4). In contrast, the secondary alcohol hexanol-3 can be selectively transformed to hexanone-3 with a rather substantial yield of 58% (entry 7). Cyclic alcohols are also suitable substrates for the oxidation by the **1**/TBHP system, providing maximum 16% and 48% yields of cyclohexanone and cyclooctanone, when using cyclohexanol and cyclooctanol, respectively. All the yield values also depend on the relative amount of TBHP, reaction temperature and time (Table 5, entries 5–13).

3.3. Oxidation of glycerol to dihydroxyacetone

As has already been mentioned, the selective and atom-efficient oxidation of glycerol (GLY) constitutes a difficult task to achieve due to its high reactivity, i.e. its easy oxidative degradation to give formaldehyde, formic acid and carbon dioxide, and the facile subsequent oxidation of primary formed products such as DHA. These limitations explain the very modest yields of the target products (usually not exceeding 15%), low selectivities and poor mass balances that are observed in most of the catalytic systems for the oxidation of glycerol [49–55].

In the present work, the homogeneous oxidation of glycerol to dihydroxyacetone (DHA) with complex **1** was undertaken at low temperatures (25–70 °C) in H_2O/MeCN medium, and the action of various oxidizing agents was screened. The selected results are summarized in Table 6.

In contrast to "simple" alcohols (isopropanol and propanol) used as models, the selective and efficient oxidation of glycerol itself by TBHP is much more difficult to realize. Thus, at ambient temperature (25 °C), only 2.5% conversion of GLY is achieved after 3 h of reaction with selectivity to DHA of 88% (Table 6, entry 1). An increase in temperature to 50 °C leads to the similar DHA yield of ca. 2% (entry 2), which is obtained, however, at a shorter reaction time (0.5 h). At a more prolonged reaction time, increased temperature, and in the presence of a catalyst promoter (HCl) and a higher amount of TBHP (entry 3), only 6.0% conversion of GLY is reached with selectivity to DHA of 90%. The promoting role of a base in glycerol oxidation has been established in various heterogeneous systems [56–60]. In this work, we have found that the presence of base (Na_2CO_3) also accelerates the reaction (entry 4) leading, after 0.5 h, to a slightly higher GLY conversion (8.5%) and DHA yield (7.5%). Further optimization of oxidations with TBHP did not allow us to obtain substantially better results.

As an alternative oxidizing agent, we have also tested aqueous hydrogen peroxide (Table 6, entries 5–8). The application of this reagent for the oxidation of glycerol was previously limited almost exclusively to heterogeneous catalytic systems [75–78]. Under our reaction conditions, H_2O_2 appears to be a more powerful oxidant leading to 15% conversion of GLY, already after 1 h of reaction at 25 °C (entry 5). This corresponds to a selectivity to DHA of 51% that is rather low due to the formation of formic and hydroxyacetic acids as by-products, detected by GS–MS analyses. The extension of the reaction time to 18 h does not have a substantial effect, resulting in a slightly higher GLY conversion (18%) with a comparable selectivity (49%) (entry 6 vs. 5). Aiming at avoiding the over-oxidation of GLY and increasing the selectivity toward DHA, we have used a tenfold reduced amount of hydrogen peroxide, what corresponds to the decrease in the H_2O_2/GLY molar ratio from 1:0.5 to 1:5. As a result, the reaction was slower and allowed to obtain after 4 h the selectivity to DHA of 96%, with GLY conversion of 2.5% (entry 7). This conversion can be increased up to 7.5% on prolonging the reaction time to 30 h (entry 8), showing also the high selectivity to DHA (93%). One should mention that in the latter case (entry 8), the DHA yield based on H_2O_2 is 35%, being rather substantial taking into consideration the mild reaction conditions. Interestingly, if the GLY oxidation is repeated (under the conditions of entry 8) with $CuCl_2$ as catalyst instead of complex **1**, only 11% DHA yield based on H_2O_2 is obtained. This fact reveals the particular importance of the N,O-ligands and their intricate arrangement in **1** (Scheme 1).

Potassium peroxodisulfate ($K_2S_2O_8$) is known as a powerful oxidant suitable for the efficient transformations of even inert gaseous alkanes [21–23,43]. Therefore, it was also tested for the oxidation of glycerol that, however, proceeded very slowly and non-selectively, resulting in 12% yield of DHA with selectivity of only 24% (Table 6, entry 9). Although some heterogeneous catalytic systems have been reported for the aerobic (or by molecular oxygen) oxidations of glycerol under rather mild reaction conditions, the attempted herein oxidation of GLY with air and complex **1** does not proceed to any extent. However, such a reaction can be mediated by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) radical that is a recognized mediator in the oxidations of various monoalcohols [11–14,45]. Hence, GLY can be transformed to DHA (ca. 10% yield)

Table 6
Homogeneous oxidation of glycerol (GLY) to dihydroxyacetone (DHA) catalyzed by complex **1**.[a]

Entry	GLY (mmol)	Oxidant (mmol)	Temperature (°C)	Time (h)	Conversion of GLY (%)	Yield of DHA[b] (%)	Selectivity to DHA (%)
1	2.5	TBHP (5.0)	25	3	2.5	2.2	88
2	1.0	TBHP (2.0)	50	0.5	2.7	2.3	85
3[c]	1.0	TBHP (4.0)	70	6	6.0	5.4	90
4[d]	1.0	TBHP (2.0)	60	0.5	8.5	7.5	88
5	2.5	H_2O_2 (5.0)	25	1	15.0	7.6	51
6	2.5	H_2O_2 (5.0)	25	18	18.0	8.8	49
7	2.5	H_2O_2 (0.5)	25	4	2.5	2.4[e]	96
8	2.5	H_2O_2 (0.5)	25	30	7.5	7.0[e]	93
9[f]	2.5	$K_2S_2O_8$ (2.5)	25	120	50.0	12.0	24
10[g]	1.0	Air/TEMPO	60	3.5	10.0	9.6	96

[a] Reaction conditions (unless stated otherwise): GLY (5 M in H_2O), compound **1** (5.0 μmol; 0.15 mL H_2O solution), TBHP (70% in H_2O) or H_2O_2 (35% in H_2O), with addition of H_2O (0.25 mL for entries 5 and 6; 0.5 mL for entries 1–3; 1.0 mL for entries 4, 7–9; 1.3 mL for entry 10), MeCN was added (2.8–3.8 mL) to reach the total volume (5.0 mL) of the reaction mixture.
[b] Molar yield (%) [moles of DHA/100 mol of GLY] determined by GC analysis.
[c] In the presence of HCl promoter (40 μmol; 1 M in H_2O).
[d] In the presence of Na_2CO_3 (3.0 mmol).
[e] Corresponds to molar (%) yield based on H_2O_2 of 12% (entry 7) or 35% (entry 8).
[f] In the presence of increased amount of H_2O (8.0 mL) for dissolving $K_2S_2O_8$; the total volume of the reaction solution was 11.0 mL.
[g] In the presence of **1** (10.0 μmol), TEMPO (50 μmol) and Na_2CO_3 (0.5 mmol), in air (1 atm); this reaction does not proceed in the absence of TEMPO.

with a high selectivity of 96% after 3.5 h of reaction at 60 °C (entry 10). Further increase in the reaction time does not lead to somehow better results. The selective TEMPO-mediated oxidations of GLY to ketomalonic acid [79] or DHA [80] have been reported but require the use of either the NaOCl/Br^- oxidant or electrochemical systems, respectively.

In most of the known heterogeneous systems [51–60], the oxidation of glycerol does not stop at the stage of DHA, proceeding more deeply with formation of various acid derivatives as the main products. However, DHA is an important chemical with recognized uses [51–55,81] in cosmetic industry (artificial suntans), pharmacological and nutritional compositions, and as an intermediate in organic synthesis, whose commercial production is limited to biological oxidation of GLY [81]. The formation of DHA in rather good yields, albeit with modest selectivities, has been previously achieved in the continuous aerobic oxidation of glycerol on heterogeneous metallic catalysts [57,82,83]. In our study, the obtained DHA yields are comparable to those achieved in the recently reported (i) H-transfer dehydrogenation of GLY to DHA, catalyzed by organometallic iridium complexes [84] and (ii) heterogeneous oxidation of GLY by the Au/CeO_2/O_2 system [85]. However, those processes exhibited significantly lower selectivities to DHA in comparison with our work.

4. Conclusions

In the present study, we have shown that the combination of the hydrosoluble tetracopper(II) complex **1** with *tert*-butyl hydroperoxide oxidant gives rise to a versatile system for the oxidative functionalization of various substrates that include alkanes, alcohols and glycerol. A very interesting feature of this system consists in unusual product distribution patterns and selectivity parameters obtained when using different types of alkane substrates. In particular, the values of regio-, bond and stereoselectivity parameters in the **1**/TBHP system indicate that the oxidations can possibly proceed in a hydrophobic pocket (cleft) containing some intermediate copper species; their nature is still to be established. This contrasts significantly to the previously studied **1**/H_2O_2 system [42], wherein hydroxyl radicals play a crucial role in alkane oxygenations. Another difference concerns the fact that alkane oxidations with catalyst **1** and TBHP do not require the addition of an acid promoter, which is typically needed to activate **1** in the oxidations with H_2O_2 [40–42]. The absence of an acid promoter eventually led to the preservation of an original structure of complex **1**, with strongly hindered copper-containing reaction centers. As a consequence, the system exhibits a noticeable selectivity in the alkane oxidations.

The work also shows that the **1**/TBHP system is suitable for the selective oxidation of secondary alcohols to the corresponding ketones, leading to product yields up to 82% and catalyst turnover numbers up to 1200 (for isopropanol oxidation). In addition, these reactions can proceed in the absence of MeCN solvent. The primary alcohols appear to be more inert (maximum 22% product yield in the oxidation of propanol), and their oxidations are less selective.

Moreover, we have extended the substrate versatility of catalyst **1** to the oxidation of glycerol, thus providing one of the first examples (see [78,86]) of its *homogeneous* metal-catalyzed oxidation. In spite of the difficulties in achieving the selective transformation of glycerol to dihydroxyaldehyde under mild conditions, all the tested systems (**1**/H_2O_2, **1**/TBHP and **1**/Air/TEMPO) are rather promising and exhibit different and interesting features. When operating with an excess of GLY, the combination of **1** with H_2O_2 appears to be particularly advantageous in terms of selectivity and oxidant efficiency. However, further optimization of all these systems to envisage higher conversions of GLY should be undertaken.

These and other research lines are planned to be explored in future developments, aiming also at the search for new hydrosoluble metal catalysts and efficient systems thereof for the selective oxidative transformations of alkanes, alcohols and glycerol into valuable chemicals.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.03.017.

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