

# Alkane hydroperoxidation with peroxides catalysed by copper complexes

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Various copper(I) and copper(II) derivatives, both "simple" ones (copper acetate, perchlorate and a complex with CH<sub>3</sub>CN) and compounds containing *N,O*-chelating ligands, catalyse very efficient (turnover numbers attain 2200) oxidation of saturated hydrocarbons with peroxyacetic acid (PAA) or *tert*-butyl hydroperoxide (TBHP) in acetonitrile solution at 60 °C. Alkyl hydroperoxide, alcohol and ketone are formed, the main product being an alkyl hydroperoxide in the oxidation with PAA and an alcohol for the case of TBHP. It has been proposed that the oxidation with PAA is induced *via* the attack of species *r*<sup>•</sup> [HO<sup>•</sup> or CH<sub>3</sub>C(=O)O<sup>•</sup>] on the alkane, RH. A competitive attack of *r*<sup>•</sup> on the solvent, CH<sub>3</sub>CN, also occurs. It has been assumed that in the case of the reaction catalysed by complex Cu(CH<sub>3</sub>CN)<sub>4</sub>BF<sub>4</sub>, copper is present mainly in the form of Cu<sup>+</sup> cation, and the rate-limiting step of the oxidation process is the formation of *r*<sup>•</sup> *via* reaction (1): CH<sub>3</sub>C(=O)OOH + Cu<sup>+</sup> → CH<sub>3</sub>C(=O)O<sup>•</sup> + HO<sup>-</sup> + Cu<sup>2+</sup> or/and CH<sub>3</sub>C(=O)OOH + Cu<sup>+</sup> → CH<sub>3</sub>C(=O)O<sup>-</sup> + HO<sup>•</sup> + Cu<sup>2+</sup> with initial rate  $W_1 = k_1[\text{PAA}][\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4]$  and  $k_1 = 1.7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  at 60 °C. The activity of the Cu-catalyst is dramatically changed on a small modification of *N,O*-chelating ligands in the catalyst.

## Introduction

Oxidative activation of various C–H compounds including very inert alkanes is an important field of contemporary metal-complex catalysis.<sup>1</sup> Copper complexes are known to catalyse benzylic and allylic oxidations by alkyl hydroperoxides and peresters.<sup>2</sup> The allylic oxidation of hydrocarbons containing double bonds (the Kharasch–Sosnovsky reaction) is used for the synthesis of allylic esters.<sup>3</sup> Much less is known about copper-catalysed oxidations of completely saturated hydrocarbons.<sup>1c,d,4</sup> It should be noted that copper complexes also catalyse efficient oxidations of some other organic compounds<sup>5</sup> such as alcohols<sup>6</sup> and aromatics.<sup>7</sup> It is important to emphasize that certain oxidizing enzymes contain copper ions<sup>8a-f</sup> which are often surrounded by *N,O*-chelating ligands.<sup>8g-n</sup> Hydroperoxides formed by the oxidation of C–H bonds in proteins

and lipoproteins, particularly with copper ion participation, play an important role in the living cell metabolism.<sup>9</sup>

Alkyl hydroperoxides<sup>10</sup> and peroxy acids<sup>11</sup> are widely used as oxidants in metal-catalysed functionalization of hydrocarbons.<sup>1</sup> They are the most important oxidizing reagents in organic catalytic chemistry after molecular oxygen and hydrogen peroxide.

## Results and discussion

We have found that various copper complexes are very efficient catalysts in alkane oxidations by peroxyacetic acid (PAA). The reactions were carried out in acetonitrile solution at 60 °C. Table 1 demonstrates that under these conditions certain salts of transition metals exhibit relatively low catalytic activity.

**Table 1** Cyclohexane oxidation with peroxyacetic acid catalysed by various metal complexes<sup>a</sup>

Entry	Catalyst	Time, h	Product concentration (mol dm <sup>-3</sup> )			TON
			Cyclohexyl hydroperoxide	Cyclohexanol	Cyclohexanone	
1	None	3	0.0008	0	0	—
2	Ni(ClO <sub>4</sub> ) <sub>2</sub>	2	0.0006	0	0	(11)
3	Co(ClO <sub>4</sub> ) <sub>2</sub>	2	0.0018	0	0	36
4	Fe(ClO <sub>4</sub> ) <sub>3</sub>	2	0.0014	0	0	28
5	Mn(ClO <sub>4</sub> ) <sub>2</sub>	2	0.0014	0	0	28
6	RhCl <sub>3</sub>	2	0.0007	0	0	(14)
7	Cu(MeCN) <sub>4</sub> BF <sub>4</sub> ( <b>1</b> )	2	0.0340	0.0050	0.0050	890 <sup>b</sup>
8	Cu(MeCN) <sub>4</sub> BF <sub>4</sub> ( <b>1</b> ) <sup>c</sup>	3	0.0130	0.0030	0.0030	1900
9	Cu(OAc) <sub>2</sub> ( <b>2</b> )	2	0.0270	0.0040	0.0040	708
10	Cu(ClO <sub>4</sub> ) <sub>2</sub> ( <b>3</b> )	2	0.0160	0.0020	0.0040	440
11	Complex <b>4</b>	2	0.0180	0.0030	0.0030	480
12	Complex <b>5</b>	2	0.0010	0.0020	0.0022	126 <sup>e</sup>
13	Complex <b>6</b> <sup>d</sup>	2		0.0007	0.0008	30

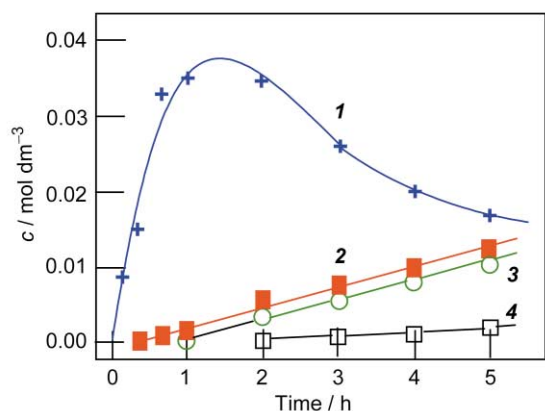
<sup>a</sup> Conditions: Total volume of the reaction solution was 5 mL; solvent acetonitrile; 60 °C; cyclohexane, 0.46 mol dm<sup>-3</sup>; PAA, 0.4 mol dm<sup>-3</sup>; catalyst  $5 \times 10^{-5}$  mol dm<sup>-3</sup>. <sup>b</sup> Additionally, CyOAc (0.0005 mol dm<sup>-3</sup>) has been also found. <sup>c</sup> Concentration of catalyst was  $1 \times 10^{-5}$  mol dm<sup>-3</sup>.

<sup>d</sup> Concentrations of the products were determined only after PPh<sub>3</sub> addition. <sup>e</sup> Additionally, CyOAc (0.0011 mol dm<sup>-3</sup>) has been also found.

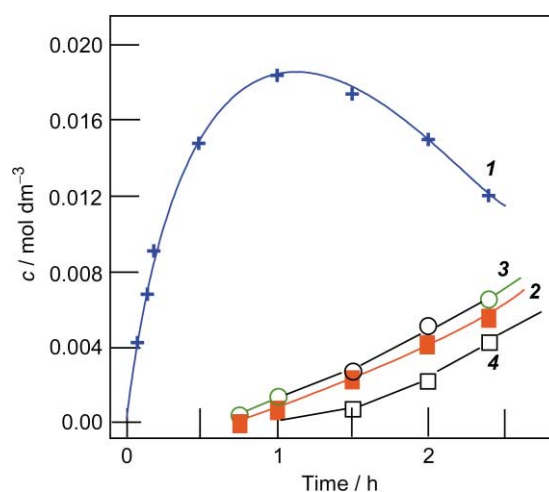
Indeed, the oxidations catalysed by cobalt(II), manganese(II) and iron(III) perchlorates (entries 3, 4, 5) give oxygenates in concentrations that only two times exceed the concentration found for the blank experiment (entry 1). These concentrations are practically equal to the blank in the case of nickel and rhodium catalysts (entries 2 and 6). Copper derivatives are in striking contrast with the metals described above and give very high turnover numbers (that is numbers of product moles per one mole of a catalyst; TONs) in such oxidations.

In our determinations of oxidation products we used a very simple method which we invented and used in our previous works on alkane oxidations.<sup>1c,e,12</sup> This method is based on comparison of the chromatograms of the reaction solution made before and after the treatment of the sample with triphenylphosphine. If an excess of solid triphenylphosphine is added to a solution of cyclohexane oxidation products before the GC analysis, the resulting chromatogram in many cases differs drastically from that of a sample not subjected to the reduction with PPh<sub>3</sub>. Such results are due to the fact that the mixture of products contains cyclohexyl hydroperoxide as the main component. After treatment of the reaction solution with PPh<sub>3</sub>, the GC analysis will give the amount of cyclohexanone which corresponds to the real concentration of this product in the reaction solution. The amount of the cyclohexanol obtained after the reduction with PPh<sub>3</sub> will give us the sum of real concentrations of the cyclohexyl hydroperoxide and the cyclohexanol. Thus, by comparing the data of the chromatographic analysis of the reaction solution before and after reduction with triphenylphosphine, we can estimate quantitatively the amounts of the cyclohexyl hydroperoxide, really present in the solution at a given moment. One of the merits of this method is the possibility to estimate the concentration of the alkyl hydroperoxide formed from the alkane in the presence of an excess of an oxidant (hydrogen peroxide, alkyl hydroperoxide, peroxy acid or metal peroxide). It should be emphasized that the method described above is not a simple "quenching of the reaction" (indeed, studies which determine alcohol and ketone concentrations only after addition of PPh<sub>3</sub> give absolutely no information about the existence or non-existence of the corresponding alkyl hydroperoxides in the solutions).

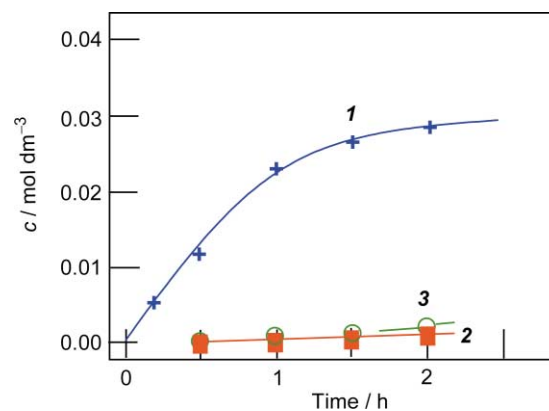
In the present work, comparison of chromatograms obtained for the samples before and after the reduction with triphenylphosphine demonstrated that the main products of alkane oxidations with PAA catalysed by copper complexes are alkyl hydroperoxides. Figs. 1–4 show the accumulation of all oxygenates with time. It can be seen that the reactions begin from the formation of cyclohexyl hydroperoxide, CyOOH, which then



**Fig. 1** Accumulation of cyclohexyl hydroperoxide (curve 1), cyclohexanone (curve 2) and cyclohexanol (curve 3) as well as cyclohexyl acetate (curve 4) in the reaction of cyclohexane (0.46 mol dm<sup>-3</sup>) with PAA (0.8 mol dm<sup>-3</sup>, as 32% solution in CH<sub>3</sub>COOH) in MeCN at 60 °C catalysed by complex [Cu(CH<sub>3</sub>CN)<sub>4</sub>]BF<sub>4</sub> (5 × 10<sup>-5</sup> mol dm<sup>-3</sup>). Concentrations of cyclohexanone and cyclohexanol were measured by GC before and after the reduction of the reaction mixture with PPh<sub>3</sub>.



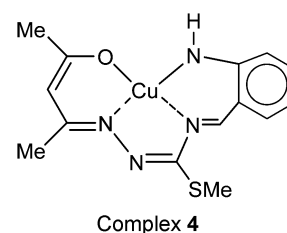
**Fig. 2** Accumulation of cyclohexyl hydroperoxide (curve 1), cyclohexanone (curve 2), cyclohexanol (curve 3) and cyclohexyl acetate (curve 4) in the reaction of cyclohexane (0.46 mol dm<sup>-3</sup>) with PAA (0.8 mol dm<sup>-3</sup>) in MeCN at 60 °C catalysed by complex Cu(ClO<sub>4</sub>)<sub>2</sub> (5 × 10<sup>-5</sup> mol dm<sup>-3</sup>). Concentrations of cyclohexanone and cyclohexanol were measured by GC before and after the reduction of the reaction mixture with PPh<sub>3</sub>.

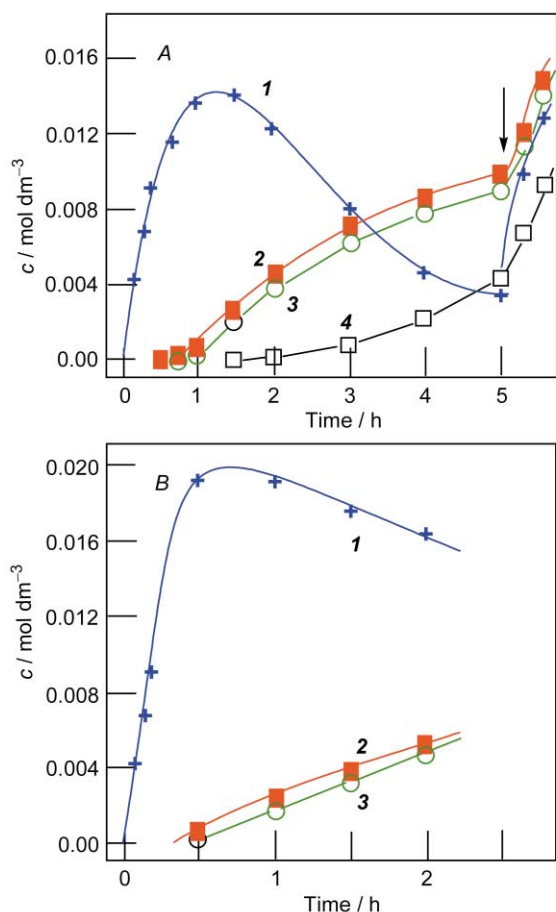


**Fig. 3** Accumulation of cyclohexyl hydroperoxide (curve 1), cyclohexanone (curve 2) and cyclohexanol (curve 3) in the reaction of cyclohexane (0.46 mol dm<sup>-3</sup>) with PAA (0.8 mol dm<sup>-3</sup>) in MeCN at 60 °C catalysed by complex Cu(OAc)<sub>2</sub> (5 × 10<sup>-5</sup> mol dm<sup>-3</sup>). Concentrations of cyclohexanone and cyclohexanol were measured by GC before and after the reduction of the reaction mixture with PPh<sub>3</sub>.

gradually decomposes to produce cyclohexanol and cyclohexanone (the maximum rate of the stable product accumulation coincides with the maximum of CyOOH concentration which is most clearly seen in Fig. 4A). There is a difference in shapes for the kinetic curves. Thus, it can be concluded that when Cu(ClO<sub>4</sub>)<sub>2</sub> is used as a catalyst under conditions described in the caption to Fig. 2, one is able to obtain almost pure cyclohexyl hydroperoxide if the reaction time is not longer than 40 min. The catalysis with Cu(OAc)<sub>2</sub> is less selective.

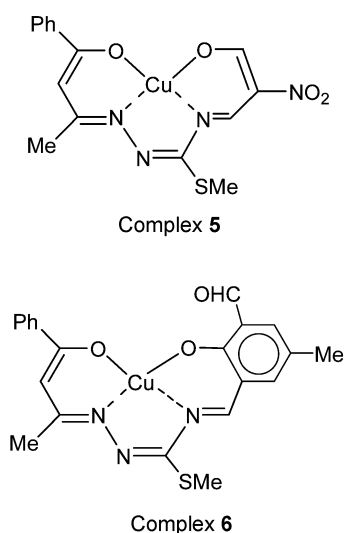
Copper(II) complexes **4**, **5** and **6** with chelating *N,O*-ligands also containing sulfur can be considered as models of copper derivatives of certain amino acids. It turned out that copper(I) complex **1** containing acetonitrile molecules as ligands exhibits the highest catalytic activity (entries 7 and 8) attaining TON =





**Fig. 4** Accumulation of cyclohexyl hydroperoxide (curve 1), cyclohexanone (curve 2), cyclohexanol (curve 3) and cyclohexyl acetate (curve 4) in the reaction of cyclohexane ( $0.46 \text{ mol dm}^{-3}$ ) with PAA (graph A:  $0.4 \text{ mol dm}^{-3}$ ; graph B:  $0.8 \text{ mol dm}^{-3}$ ) in MeCN at  $60^\circ\text{C}$  catalysed by complex 4 ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ). Concentrations of cyclohexanone and cyclohexanol were measured by GC before and after the reduction of the reaction mixture with  $\text{PPh}_3$ . At the moment denoted by an arrow an additional amount of PAA ( $0.4 \text{ mol dm}^{-3}$ ) was added.

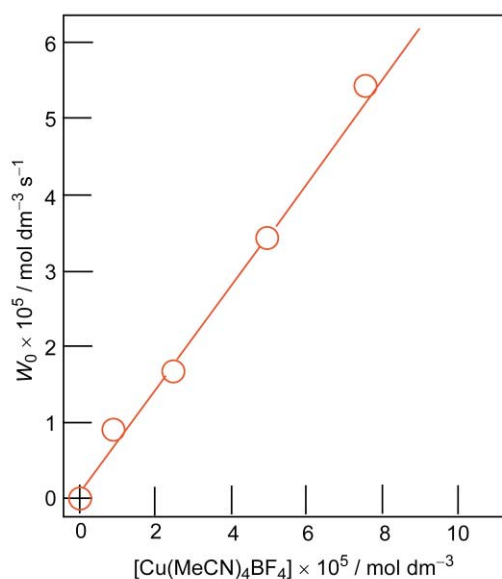
1900. Copper(II) acetate and perchlorate are a bit less efficient catalysts (entries 9 and 10, respectively). It is noteworthy that activities of complexes containing chelating ligands depend dramatically on the ligand structure. Thus a complex containing a copper(II) ion coordinated to three nitrogens and only one oxygen catalyses the oxidation (entry 11) with TON comparable with those obtained for simple inorganic derivatives (entries 9 and 10). Compound 5 which contains a ligand surrounding



copper symmetrically with two nitrogens and two oxygens gives relatively lower TON (entry 12). Surprisingly, a similar complex 6 (which however differs from 5 by its geometry) exhibited only very moderate activity (entry 13).

It follows from comparison of graphs A and B in Fig. 4 that the selectivity can be increased by using a higher concentration of PAA. The catalyst is not destroyed in the course of the reaction, and if a new portion of PAA is added to the reaction solution the oxidation begins with approximately the same rate (Fig. 4A). This means that the TON and alkane conversion parameters can be easily increased by adding PAA portion by portion. It should be noted that in these oxidations of very inert alkanes, we obtained yields of oxygenates up to 10% based on starting cyclohexane and 14% based on initial PAA, however to optimise the yields was not the aim of this study.

The rate dependence of the cyclohexane oxygenation catalysed by compound  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$  (1) is first order for the initial 1 complex (Fig. 5). First order has been also found for cyclohexane at relatively low concentrations; however at relatively high cyclohexane concentrations the rate dependence is zero order (Fig. 6).



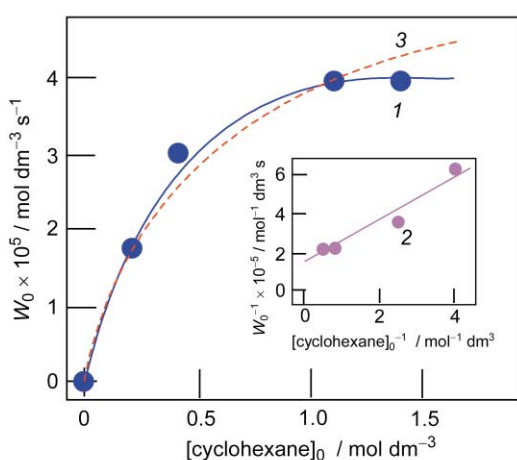
**Fig. 5** Plot of the initial rate of the cyclohexane ( $0.46 \text{ mol dm}^{-3}$ ) oxidation by PAA ( $0.8 \text{ mol dm}^{-3}$ ) versus concentration of  $\text{Cu}(\text{MeCN})_4\text{BF}_4$  used as a catalyst (in acetonitrile,  $60^\circ\text{C}$ ). The reaction rates were calculated from the slopes of kinetic curves of product accumulation in the initial period of the reaction and concentrations of cyclohexanone and cyclohexanol were measured by GC only after the reduction of the reaction mixture with  $\text{PPh}_3$ .

In order to get additional mechanistic information on this reaction, we studied the oxidation of certain higher alkanes. The results are summarized in Table 2. Corresponding selectivity parameters are also given for certain other systems known to oxidize alkanes via free-radical mechanism (the  $\text{O}_2\text{-H}_2\text{O}_2\text{-}n\text{Bu}_4\text{NVO}_3\text{-PCA}$  reagent)<sup>13,14</sup> and to operate without involvement of free radicals: the  $\text{H}_2\text{O}_2\text{-}[\text{LMn}^{\text{IV}}(\text{O})_3\text{Mn}^{\text{IV}}\text{L}](\text{PF}_6)_2\text{-MeCO}_2\text{H}$  system<sup>11d,15</sup> and the  $\text{H}_2\text{O}_2\text{-}m\text{-CPBA-Co}(\text{ClO})_4$  combination.<sup>16</sup> It can be seen that selectivity parameters for the Cu-catalysed oxidations of *n*-hexane and isooctane by PAA are noticeably lower than that obtained for “non-radical” systems. These parameters are close (though a bit higher) to the corresponding values known for the  $\text{O}_2\text{-H}_2\text{O}_2\text{-}n\text{Bu}_4\text{NVO}_3\text{-PCA}$  reagent which operates via the formation of free hydroxyl radicals.<sup>13,14</sup> The Cu-catalysed oxidation occurs without retention of configuration at *tert*-carbons (compare corresponding parameters in Table 2 for oxidations of *cis*- and *trans*-DMCH) which is in agreement with free-radical mechanism of the reaction.

**Table 2** Selectivity parameters in the Cu-catalysed oxidation with PAA and *tert*-butyl hydroperoxide<sup>a</sup>

Entry	Substrate	Oxidant	Catalyst	Selectivity	
1	<i>n</i> -Hexane	PAA	Cu(MeCN) <sub>4</sub> BF <sub>4</sub>	<b>C(1) : C(2) : C(3)<sup>b</sup></b> 1 : 13 : 11	
2			Cu(ClO <sub>4</sub> ) <sub>2</sub>	1 : 14 : 10	
3			Cu(OAc) <sub>2</sub>	1 : 12 : 13	
4			Complex 4	1 : 10 : 10	
5			Complex 5	1 : 15 : 12	
6			H <sub>2</sub> O <sub>2</sub>	<i>n</i> Bu <sub>4</sub> NVO <sub>3</sub> -PCA <sup>c</sup>	1 : 8 : 7
7	<i>n</i> -Heptane	<i>t</i> -BuOOH	Cu(MeCN) <sub>4</sub> BF <sub>4</sub>	<b>C(1) : C(2) : C(3) : C(4)<sup>a</sup></b> 1 : 14 : 9 : 13	
8			Complex 4	1 : 16 : 9 : 13	
9			H <sub>2</sub> O <sub>2</sub>	<i>n</i> Bu <sub>4</sub> NVO <sub>3</sub> -PCA <sup>c</sup>	1 : 6 : 6 : 5
10			[LMn <sup>IV</sup> (O) <sub>3</sub> Mn <sup>IV</sup> L](PF <sub>6</sub> ) <sub>2</sub> -MeCO <sub>2</sub> H <sup>d</sup>	1 : 46 : 35 : 34	
11			<i>m</i> -CPBA	Co(ClO <sub>4</sub> ) <sub>4</sub> <sup>e</sup>	1 : 104 : 128 : 126
12	Isooctane <sup>g</sup>	PAA	Cu(MeCN) <sub>4</sub> BF <sub>4</sub>	<b>1° : 2° : 3°<sup>f</sup></b> 1 : 1.7 : 12.5	
13			Cu(ClO <sub>4</sub> ) <sub>2</sub>	1 : 2.0 : 22.2	
14			Complex 4	1 : 1.5 : 11.5	
15			Complex 5	1 : 3.9 : 13.0	
16			H <sub>2</sub> O <sub>2</sub>	<i>n</i> Bu <sub>4</sub> NVO <sub>3</sub> -PCA <sup>c</sup>	1 : 4.0 : 9.0
17			[LMn <sup>IV</sup> (O) <sub>3</sub> Mn <sup>IV</sup> L](PF <sub>6</sub> ) <sub>2</sub> -MeCO <sub>2</sub> H <sup>d</sup>	1 : 5.0 : 50.0	
18			<i>t</i> -BuOOH	Cu(MeCN) <sub>4</sub> BF <sub>4</sub>	<b>1° : 3°</b> 1 : 41 <sup>h</sup>
19	Complex 4	1 : 34 <sup>h</sup>			
		<b><i>trans/cis</i><sup>i</sup></b>			
20	<i>cis</i> -DMCH <sup>j</sup>	PAA	Complex 4	0.66	
21		H <sub>2</sub> O <sub>2</sub>	<i>n</i> Bu <sub>4</sub> NVO <sub>3</sub> -PCA <sup>c</sup>	0.7	
22	<i>trans</i> -DMCH <sup>j</sup>	<i>m</i> -CPBA	[LMn <sup>IV</sup> (O) <sub>3</sub> Mn <sup>IV</sup> L](PF <sub>6</sub> ) <sub>2</sub> -MeCO <sub>2</sub> H <sup>d</sup>	0.34	
23			Co(ClO <sub>4</sub> ) <sub>4</sub> <sup>e</sup>	0.0005	
24			PAA	Complex 4	0.45
25			H <sub>2</sub> O <sub>2</sub>	<i>n</i> Bu <sub>4</sub> NVO <sub>3</sub> -PCA <sup>c</sup>	0.8
26			[LMn <sup>IV</sup> (O) <sub>3</sub> Mn <sup>IV</sup> L](PF <sub>6</sub> ) <sub>2</sub> -MeCO <sub>2</sub> H <sup>d</sup>	4.1	
27	<i>m</i> -CPBA	Co(ClO <sub>4</sub> ) <sub>4</sub> <sup>e</sup>	61		

<sup>a</sup> The parameters were calculated based on concentrations of isomeric alcohols formed in the reaction and were measured after the reduction of the reaction solution with PPh<sub>3</sub>. <sup>b</sup> Parameter C(1) : C(2) : C(3) : C(4) is normalized (*i.e.*, calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogen atoms in positions 1, 2, 3, and 4 of the hydrocarbon chain, respectively. <sup>c</sup> PCA is pyrazine-2-carboxylic acid; for this system, see Refs. 1c–e, 13, 14. <sup>d</sup> L is 1,4,7-trimethyl-1,4,7-triazacyclononane; for this system, see Refs. 11d, 15. <sup>e</sup> *m*-CPBA is *m*-chloroperoxybenzoic acid; for this system, see Ref. 16. <sup>f</sup> Parameter 1° : 2° : 3° is normalized relative reactivities of hydrogen atoms at primary, secondary and tertiary carbons, respectively. <sup>g</sup> 2,2,4-Trimethylpentane. <sup>h</sup> Secondary alcohols have not been found. <sup>i</sup> This parameter is the *trans/cis* ratio of isomers of *tert*-alcohols formed in the oxidation of *cis*- or *trans*-1,2-dimethylcyclohexane. <sup>j</sup> 1,2-Dimethylcyclohexane.

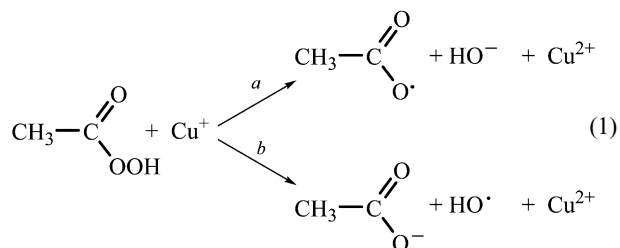


**Fig. 6** Plot of the initial rate of the cyclohexane oxidation by PAA (0.8 mol dm<sup>-3</sup>) catalysed by Cu(MeCN)<sub>4</sub>BF<sub>4</sub> (5 × 10<sup>-5</sup> mol dm<sup>-3</sup>) versus initial concentration of cyclohexane (curve 1) and the linear anamorphosis of this dependence (curve 2) obtained using eqn. (4). Curve 3 shows the simulated dependence of *W*<sub>0</sub> on [cyclohexane]<sub>0</sub> calculated using eqn. (4) and parameters for this equation taken from line 2. The reaction was carried out in acetonitrile at 60 °C. The reaction rates were calculated from the slopes of kinetic curves of product accumulation in the initial period of the reaction and concentrations of cyclohexanone and cyclohexanol were measured by GC only after the reduction of the reaction mixture with PPh<sub>3</sub>.

It should be noted that the yield of oxygenates is lower than PAA consumption (see, for example, Fig. 1). Peroxy acids are

known to decompose “non-productively” to give molecular oxygen<sup>17a</sup> and decarboxylation products.<sup>17b</sup>

Since cyclohexane is not known to form complexes with copper ions, the fact of its oxidation in the system under discussion testifies that an intermediate species inducing the process is generated *via* a catalytic decomposition of PAA. We can assume that in the first step of the reaction copper ions induce generation of free radicals from PAA. These may be products of homolytic splitting the O–O bond in PAA, that is radicals HO<sup>•</sup> or <sup>•</sup>OC(=O)CH<sub>3</sub>.



Both radicals then attack the hydrocarbon abstracting its hydrogen atom which leads to the formation of an alkyl radical, R<sup>•</sup>. The latter reacts rapidly with atmospheric molecular oxygen to produce a peroxy radical, ROO<sup>•</sup>, which can further add either a hydrogen atom or electron [from copper(i) derivative] followed by the proton addition. The hydrogen atom can be abstracted from the other alkane molecule since the radical

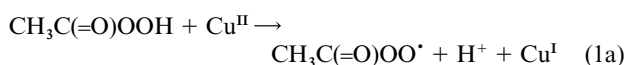
**Table 3** Cyclohexane oxidation with *tert*-butyl hydroperoxide catalysed by copper complexes<sup>a</sup>

Entry	Catalyst	Time, h	Product concentration (mol dm <sup>-3</sup> )			TON
			Cyclohexyl hydroperoxide	Cyclohexanol	Cyclohexanone	
1	Cu(MeCN) <sub>4</sub> BF <sub>4</sub>	5	0.005	0.075	0.030	2200
2	Complex <b>4</b>	5	0.007	0.030	0.044	1760

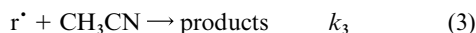
<sup>a</sup> Conditions: Total volume of the reaction solution was 5 mL; solvent acetonitrile; 60 °C; cyclohexane, 0.92 mol dm<sup>-3</sup>; *t*-BuOOH, 0.78 mol dm<sup>-3</sup>; catalyst, 5 × 10<sup>-5</sup> mol dm<sup>-3</sup>.

chain process at elevated temperature is possible in small extent for the case of higher alkanes<sup>13b</sup> (ROO<sup>•</sup> + RH → ROOH + R<sup>•</sup>). In both cases the alkyl hydroperoxide, ROOH, is formed. This compound decomposes slowly (copper complexes presumably catalyse this process) to the more stable corresponding alcohol and ketone (see Fig. 1).

A Cu(II) derivative can be transformed into a Cu(I) complex *via* the interaction with PAA according to equation:



As it has been mentioned above, the data of Fig. 6 show that with increase of the cyclohexane concentration the order of the oxidation reaction decreases from unity to zero. Taking into account the above proposal about the radical nature of oxidation-inducing species *r*<sup>•</sup> (where *r*<sup>•</sup> is HO<sup>•</sup> or CH<sub>3</sub>CO<sup>•</sup>O) we can conclude that the data of Fig. 6 are in agreement with the assumption<sup>13</sup> concerning competition between cyclohexane, RH, and the solvent, CH<sub>3</sub>CN, in the reaction with an active oxidising species:



The analysis of competitive reactions (2) and (3) leads to the following kinetic equation for the stationary RH oxidation rate:

$$-\frac{d[\text{RH}]}{dt} = \frac{W_i}{1 + \frac{k_3[\text{CH}_3\text{CN}]}{k_2[\text{RH}]}} \quad (4)$$

where *W*<sub>*i*</sub> is the *r*<sup>•</sup> formation rate in the catalytic PAA decomposition. Experimental parameters of Fig. 6 (curve 1) are adequately described by eqn. (4). Indeed, the dependence of the reversed RH oxidation rate on the reversed RH concentration is depicted by straight line 2. The parameters for this line calculated using the least-square method are the following: the segment cut of the *Y*-axis is equal to 1.5 × 10<sup>4</sup> mol<sup>-1</sup> dm<sup>3</sup> s, the tangent of the line slope is equal to 1.1 × 10<sup>4</sup> s. According to eqn. (4) the segment cut of the *Y*-axis is equal to 1/*W*<sub>*i*</sub>, and the tangent of the slope is equal to *k*<sub>3</sub>[CH<sub>3</sub>CN]/*k*<sub>2</sub>. Accepting [CH<sub>3</sub>CN] = 18 mol dm<sup>-3</sup> we will have at 60 °C the following parameters: *k*<sub>3</sub>/*k*<sub>2</sub> = 0.04, *W*<sub>*i*</sub> = 6.7 × 10<sup>-5</sup> mol dm<sup>-3</sup> s<sup>-1</sup> at [PAA]<sub>0</sub> = 0.8 mol dm<sup>-3</sup> and [I] = 5 × 10<sup>-5</sup> mol dm<sup>-3</sup>. Let us compare the obtained parameters with known corresponding constant ratio for the rate of interaction of HO<sup>•</sup> with CH<sub>3</sub>CN and cyclohexane: 0.012 at 25 °C. In order to extrapolate this value to the higher temperature let us assume that the difference in *k*<sub>3</sub> and *k*<sub>2</sub> values is due only to the difference in the activation energy values. In this case it follows from the ratio *k*<sub>3</sub>/*k*<sub>2</sub> = 0.012 at 25 °C that *E*<sub>3</sub> - *E*<sub>2</sub> = 11 kJ mol<sup>-1</sup> and consequently *k*<sub>3</sub>/*k*<sub>2</sub> = 0.019 at 60 °C. This means that the *k*<sub>3</sub>/*k*<sub>2</sub> value for the Cu-catalysed oxidation with PAA is only two times higher than the same parameter for the reaction with hydroxyl radicals, and we cannot choose definitely between routes *a* and *b* of reaction (1). One can assume that results obtained testify that reactivities of

HO<sup>•</sup> and CH<sub>3</sub>C(=O)O<sup>•</sup> radicals in the competitive pair are close.

The rate of reaction (1) should be written as follows:

$$W_i = W_i = k_1[\text{PAA}][\text{I}] \quad (5)$$

The initial rate *W*<sub>*i*</sub> of *r*<sup>•</sup> generation for the system under investigation has been determined above. In order to calculate the rate constant of this reaction we need to know the stationary concentration of Cu<sup>+</sup> ions. In order to estimate this constant let us use the following data. It is known from the literature<sup>18</sup> that acetonitrile stabilizes copper in the form of Cu<sup>+</sup> ions in aqueous solution, and due to this acetonitrile complex of Cu(I) is oxidized much slower by dioxygen and hydrogen peroxide in comparison with Cu<sup>+</sup>·aq. As a result, in the system under discussion copper is present mainly in the form of Cu<sup>+</sup> cation, and the rate-limiting step of the oxidation process is reaction (1). This assumption easily explains the linear dependence of the reaction rate on the concentration of complex **1**, and the rate constant of this reaction *k*<sub>1</sub> at 60 °C is 1.7 mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>.

It is necessary to note that neither *meta*-chloroperbenzoic acid (*m*-CPBA) nor hydrogen peroxide oxidize cyclohexane efficiently when the copper complexes are used as catalysts. Thus, the catalysis with compound **4** (5 × 10<sup>-5</sup> mol dm<sup>-3</sup>) gave 0.0010 mol dm<sup>-3</sup> of cyclohexanol and 0.00075 mol dm<sup>-3</sup> of cyclohexanone (as well as small amounts of cyclohexyl hydroperoxide; total TON = 35) in the experiment with *m*-CPBA at 40 °C (24 h) and only TON = 17 in the experiment with 30% H<sub>2</sub>O<sub>2</sub> (40 °C, 1 h). On the contrary, we have found that *tert*-butyl hydroperoxide very efficiently (TONs were up to 2200) oxidizes alkanes if copper derivatives are used as catalysts. A remarkable feature of this reaction is the predominant formation of alcohols as shown for the case of cyclohexane oxidation (Table 3). Determination of cyclohexanol and cyclohexanone by GC before and after the reduction with PPh<sub>3</sub> showed that, in contrast to the oxidation with PAA, the corresponding cyclohexyl hydroperoxide is formed in relatively low concentration; its maximum content was found in the beginning of the reaction (Figs. 7 and 8). The values of selectivity parameters for the oxidation with *tert*-butyl hydroperoxide (see Table 2) testify that this process occurs with participation of free radicals, most probably *t*-BuO<sup>•</sup>.

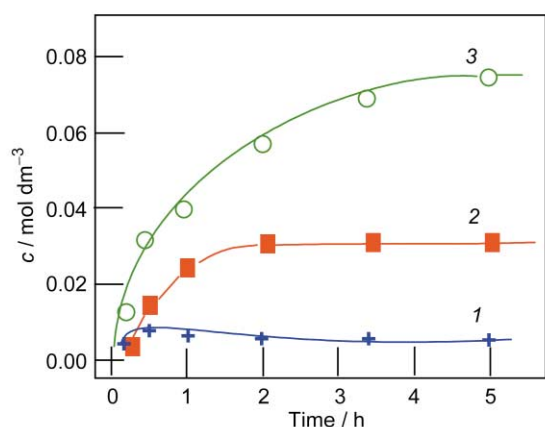
## Conclusions

Our experiments demonstrated that while “simple” copper complexes can be successfully used (after modifications and optimisation) in the preparative scale for the preparation of the solutions of alkyl hydroperoxides directly from corresponding alkanes, complexes containing chelating *N,O*-ligands can be considered as biomimetic models of copper-based enzymes. It is noteworthy that, like in Nature, relatively minor changes in the ligand's structure lead to a dramatic decrease of the catalytic activity.<sup>1c,e</sup>

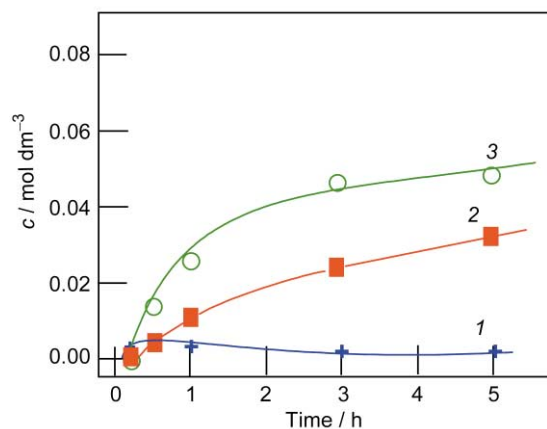
## Experimental

The oxidation experiments were carried out in MeCN at 60 °C in thermostated Pyrex cylindrical vessels with vigorous stirring.





**Fig. 7** Accumulation of cyclohexyl hydroperoxide (curve 1), cyclohexanone (curve 2) and cyclohexanol (curve 3) in the reaction of cyclohexane ( $0.92 \text{ mol dm}^{-3}$ ) with *t*-BuOOH ( $0.78 \text{ mol dm}^{-3}$ , as 70% aqueous solution) in MeCN at  $60 \text{ }^\circ\text{C}$  catalysed by  $\text{Cu}(\text{MeCN})_4\text{BF}_4$  ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ). Concentrations of cyclohexanone and cyclohexanol were measured by GC before and after the reduction of the reaction mixture with  $\text{PPh}_3$ .



**Fig. 8** Accumulation of cyclohexyl hydroperoxide (curve 1), cyclohexanone (curve 2) and cyclohexanol (curve 3) in the reaction of cyclohexane ( $0.92 \text{ mol dm}^{-3}$ ) with *t*-BuOOH ( $0.78 \text{ mol dm}^{-3}$ , as 70% aqueous solution) in MeCN at  $60 \text{ }^\circ\text{C}$  catalysed by complex **4** ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ). Concentrations of cyclohexanone and cyclohexanol were measured by GC before and after the reduction of the reaction mixture with  $\text{PPh}_3$ .

The total volume of the reaction solution was 5 mL. In a typical experiment, initially, a portion of PAA (32% solution in acetic acid, "Aldrich") was added to the solution of the catalyst and cyclohexane in acetonitrile. In order to determine concentrations of all cyclohexane oxidation products the samples of reaction solutions were analysed twice (before and after their treatment with  $\text{PPh}_3$ ) by GC (LKhM-80-6, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas argon) measuring concentrations of cyclohexanol and cyclohexanone. This method (an excess of solid triphenylphosphine is added to the samples 10–15 min before the GC analysis)<sup>16, 12</sup> allows the detection of alkyl hydroperoxides and the measurement of the real concentrations of all three products (alkyl hydroperoxide, alcohol and aldehyde or ketone) present in the reaction solution, because in many cases alkyl hydroperoxides are decomposed in the gas chromatograph to produce the corresponding alcohol and ketone.

Synthesis and characterization (elemental analysis, spectra and X-ray analysis) of complexes **4–6** is reported elsewhere.<sup>19</sup>

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