Alkane oxidation by the system 'tert-butyl hydroperoxide–[Mn₂L₂O₃][PF₆]₂ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)–carboxylic acid'

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The kinetics of cyclohexane (CyH) oxygenation with *tert*-butyl hydroperoxide (TBHP) in acetonitrile at 50 °C catalysed by a dinuclear manganese(IV) complex 1 containing 1,4,7-trimethyl-1,4,7-triazacyclononane and co-catalysed by oxalic acid have been studied. It has been shown that an active form of the catalyst (mixed-valent dimeric species 'Mn^{III}Mn^{IV}') is generated only in the interaction between complex 1 and TBHP and oxalic acid in the presence of water. The formation of this active form is assumed to be due to the hydrolysis of the Mn—O—Mn bonds in starting compound 1 and reduction of one Mn^{IV} to Mn^{III}. A species which induces the CyH oxidation is radical *tert*-BuO$^\bullet$ generated by the decomposition of a monoperoxo derivative of the active form. The constants of the equilibrium formation and the decomposition of the intermediate adduct between TBHP and 1 have been measured: $K = 7.4$ mol^{-1} dm^3 and $k = 8.4 \times 10^{-2}$ s^{-1}, respectively, at [H$_2$O] = 1.5 mol dm^{-3} and [oxalic acid] = 10^{-2} mol dm^{-3}. The constant ratio for reactions of the monomolecular decomposition of *tert*-butoxy radical (*tert*-BuO$^\bullet$ → CH$_3$COCH$_3$ + CH$_3$) and its interaction with the CyH (*tert*-BuO$^\bullet$ + CyH → *tert*-BuOH + Cy$^\bullet$) was calculated: 0.26 mol dm^{-3}. One of the reasons why oxalic acid accelerates the oxidation is due to the formation of an adduct between oxalic acid and 1 ($K \approx 10^3$ mol^{-1} dm^3). Copyright © 2007 John Wiley & Sons, Ltd.

Keywords: alkanes; alcohols; alkyl hydroperoxides; cyclohexane; cyclohexanol; homogeneous catalysis; kinetics; manganese complexes; oxidation; *tert*-butyl hydroperoxide (TBHP)

INTRODUCTION

tert-Butyl hydroperoxide (TBHP) is known as an efficient oxidizing agent for the oxygenation of alkanes and other C—H compounds[1] to alkyl hydroperoxides, ketones (aldehydes) and alcohols in reactions catalysed by complexes of ruthenium,[2] cobalt,[3] copper,[4] iron,[5] rhodium,[6] titanium and zirconium,[7] cerium,[8] cromium,[9] vanadium[10] and osmium.[11] Manganese derivatives containing in many cases chelating N-ligands are among the most active catalysts in such oxidations.[12a–o] It is interesting that rhenium complexes are less efficient in oxidations of various C—H bonds.[12p–s] Earlier we discovered that the dinuclear manganese(IV) complex [LMn(O)₃MnL](PF₆)₂ (complex 1; L is 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN) in the presence of a carboxylic acid efficiently catalyses oxidations of alkanes and other organic compounds by hydrogen peroxide[13] (refer also to reviews[14]). Preliminary results showed that TBHP can be also used in such reactions.[13d,e] In the present work, to get the information on a possible mechanism we studied in more detail the kinetics of the cyclohexane (CyH) oxidation by TBHP catalysed with 1 in acetonitrile.

To demonstrate the formation of cyclohexyl hydroperoxide (CyOOH) in CyH oxidations and to estimate its concentration in the course of the reaction we used a simple method developed by us earlier.[14a,b,15] If an excess of solid PPh₃ is added to the sample of the reaction solution *ca* 10 min prior the GC analysis, the alkyl hydroperoxide present is completely reduced to the corresponding alcohol. As a result, the chromatogram differs from that of a sample not subjected to the reduction: the alcohol peak rises, while the intensity of the ketone peak decreases. Comparing the intensities of peaks attributed to the alcohol and ketone before and after the reduction, it is possible to estimate the real concentrations of alcohol, ketone and alkyl hydroperoxide present in the reaction solution. In recent years, our method was applied by other chemists in various oxidations of C—H compounds.[16]

RESULTS AND DISCUSSION

In preliminary works, we have found that the alkane oxidation with TBHP in acetonitrile solution catalysed by complex 1 is

Complex 1

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J. Phys. Org. Chem. **2008**, 21 119–126

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119

significantly accelerated if acetic acid is added into the reaction mixture.[13d,e] In the present study, we decided to investigate first of all the effect of various carboxylic acid in this reaction. In the initial period, the reaction gives predominantly cyclohexyl hydroperoxide (for the method of its determination, see above). In our kinetic studies we were interested only in the maximum reaction rates which were measured from sum of concentrations of the products. To measure these concentrations we typically reduced the samples of the reaction solutions with PPh$_3$ and determined the amounts of cyclohexanol and cyclohexanone. This reduction leads to the most precise kinetic determinations. We have found that logarithms of maximum reaction rates linearly depend on the pK_a parameters for certain carboxylic acids (Fig. 1). It can be seen that oxalic acid is more efficient as a co-catalyst in comparison with acetic acid. Although this difference is about only four times, we used oxalic acid in all our further experiments.

Typical kinetic curves of the accumulation of the CyH oxygenation products are shown in Fig. 2. The reaction rate is significantly higher if oxalic acid is present in the solution (compare curves 1 and 2). Kinetic curves correspond to the current concentration cyclohexanone + cyclohexanol after the reduction of the reaction sample with PPh$_3$. The reaction begins slowly, and only after 1.5 h the rate attains its maximum value. In our further experiments, we measured this maximum rate. After 3 h the rate gradually decreases.

We determined the current concentration of TBHP in the course of the reaction and found that for the cases of all carboxylic acids [TBHP] decreases not more than for 10–15% (when the rate attains the maximum value), that is, it practically remains to be equal to the initial concentration of TBHP. The CyH oxidation occurs also in the absence of any carboxylic acid (curve 1, Fig. 2), however, in this case the initial slow period of the reaction is much longer. In the oxidation co-catalysed by oxalic acid the initial slow lag period of the reaction can be shorten or even removed completely if we use the reaction solution containing all the components except either TBHP or CyH and pre-treated prior the reaction at 50 °C for 1 h. If we introduce after such the pre-treatment either TBHP or CyH, respectively, we can notice
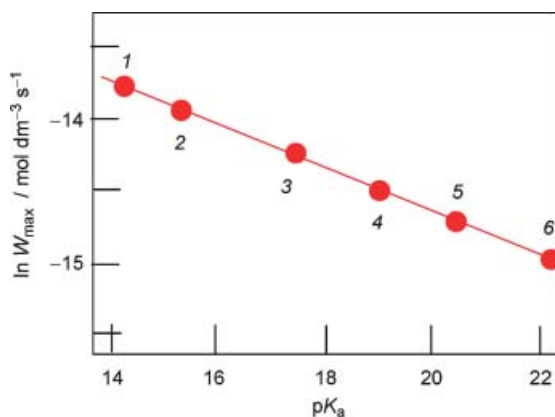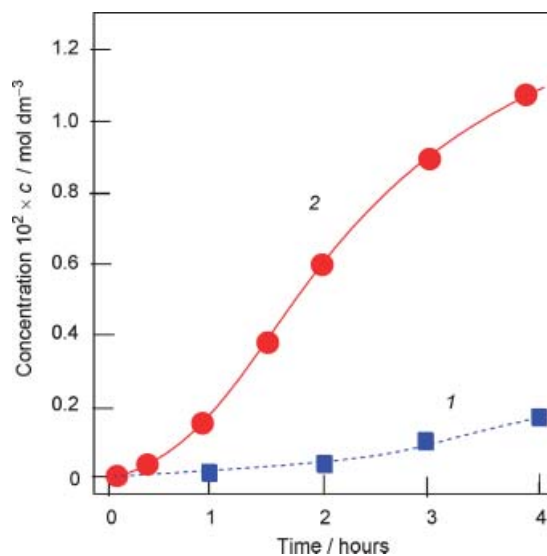

Figure 2. Kinetic curves of cyclohexanone + cyclohexanol accumulation in the cyclohexane oxidation catalysed by complex **1** (5×10^{-5} mol dm^{-3}) in the absence (curve 1) and in the presence of oxalic acid (10^{-2} mol dm^{-3}; curve 2). Conditions: [CyH]$_0$ = 0.46 mol dm^{-3}; [TBHP]$_0$ = 0.10 mol dm^{-3}; 50 °C.

that the lag period disappears (Fig. 3). In the case of other carboxylic acids shortening of the lag period can be noticed only after pre-treatment of all components without CyH and after subsequent addition of CyH. These kinetic data testify that during the initial slow period of the reaction a modification of the
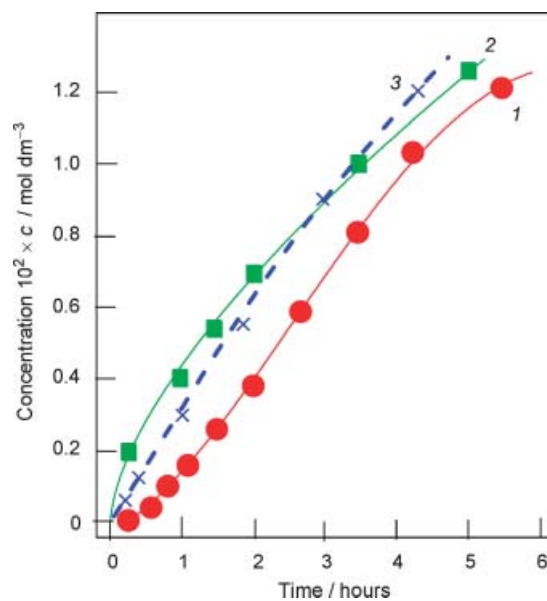

Figure 1. Dependence of ln W_{max} (where W_{max} is the maximum reaction rate attained in the beginning of the reaction) in the cyclohexane oxidation catalysed by complex **1** (5×10^{-5} mol dm^{-3}) in the presence of certain carboxylic acids (5×10^{-4} mol dm^{-3}) on the pK_a parameters of these acids: oxalic (1), malonic (2), succinic (3), glutaric (4), adipic (5) and acetic (6) acids. Conditions: [CyH]$_0$ = 0.46 mol dm^{-3}; [TBHP]$_0$ = 0.1 mol dm^{-3}; 50 °C.

Figure 3. Kinetic curves of cyclohexanone + cyclohexanol accumulation in the cyclohexane oxidation catalysed by complex **1** (5×10^{-5} mol dm^{-3}) and oxalic acid (10^{-2} mol dm^{-3}). Curve 1: all components were introduced in the initial moment (time = 0); curve 2: the reaction solution was pre-treated at 50 °C for 1 h in the absence of TBHP and after that TBHP was added at time = 0; curve 3: the reaction solution was pre-treated at 50 °C for 1 h in the absence of CyH and after that cyclohexane was added at time = 0. Conditions: [CyH]$_0$ = 0.46 mol dm^{-3}; [TBHP]$_0$ = 0.10 mol dm^{-3}; 50 °C.

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J. Phys. Org. Chem. **2008**, 21 119–126

catalyst precursor **1** occurs, and complex **1** is transformed into a new species which is more catalytically active one.

Our studies using UV–Vis spectroscopy support the conclusion about the formation of a more active in catalysis species. Figure 4 demonstrates the spectra of the reaction solution at time = 0 (curve 1) and at the moments when the reaction rate is sufficiently increased approaching to its maximum value (curve 2) and when the reaction deceases (curve 3). It can be seen that the curves differ dramatically. According to the data by Wieghardt *et al.*[17] the absorption in the region 500 nm in the spectrum 2 is due to the dimeric structure of a mixed-valent complex 'Mn^{III}Mn$^{IV'}$. This species can contain two μ-oxo bridges and also oxalate as the third bridge.[17] An increase of the oxygenation rate occurs simultaneously with the increase of the species 'Mn^{III}Mn$^{IV'}$ concentration. The subsequent decrease of the rate correlates with the disappearance of this species. Based on this observation we can assume that the complex 'Mn^{III}Mn$^{IV'}$ is the most active in the oxygenation species.

An important feature of oxalic acid as a co-catalyst was the fact that only in its presence we can observe a slow (more slow than it was under the conditions of the catalytic alkane oxidation) conversion of complex **1** to a 'Mn^{III}Mn$^{IV'}$ species even in the absence of TBHP. This fact can be due to the reducing properties of oxalic acid in contrast to the properties of other acids studied in this work. It is reasonable to assume that it is the TBHP which plays the role of a reducing agent in the catalytic process in the presence of other acids.

Our experimental data suggest that the transformation of complex **1** into the 'Mn^{III}Mn$^{IV'}$ species occurs with participation of water molecules (in the anhydrous acetonitrile solution complex **1** is stable and its optical spectrum is not changed with time). The
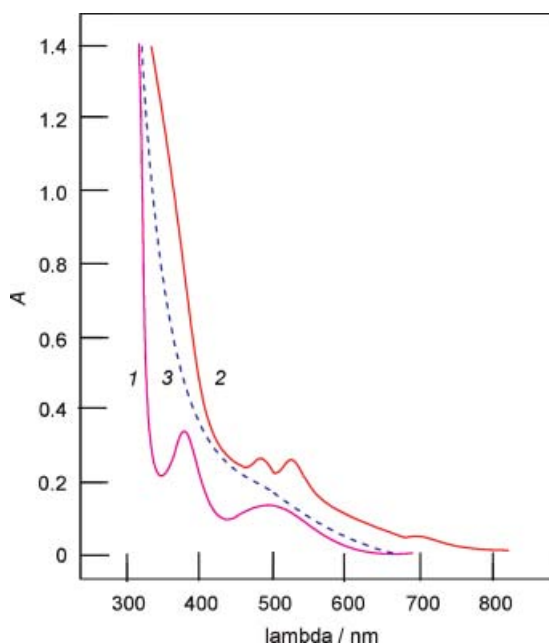
conversion **1** → 'Mn^{III}Mn$^{IV'}$ is accelerated by adding a carboxylic acid. As the rate of this transformation depends on the nature of the carboxylic acid and its concentration one can assume that the conversion of **1** includes the primary stage of the hydrolysis of the oxo bond in compound **1**. Then the reduction of one Mn^{IV} ion to produce the Mn^{III} ion occurs followed by some changes in the species structure which is a dimer as previously. The existence of the dimeric structure of the 'Mn^{III}Mn$^{IV'}$ species is supported by a similarity of the absorption spectra obtained for our system and previously published for synthesized dimeric complexes containing manganese ions.[17]

It should be noted that in our further studies, the maximum rate, W_{max}, of the cyclohexanone + cyclohexanol accumulation (after reduction with PPh$_3$) was used as a kinetic parameter of the system. The maximum rate is attained after practically complete transformation of the oxo complex **1** into the mixed-valent 'Mn^{III}Mn$^{IV'}$ species. This parameter was considered as the initial stationary reaction rate (because TBHP consumption is negligible). Such a rate corresponds to the catalysis by the mixed-valent 'Mn^{III}Mn$^{IV'}$ species which concentration is equal to the concentration of **1**. We should also emphasize that only oxalic acid has reducing properties unlike all other carboxylic acids studied here. Nevertheless, reducing ability of oxalic acid does not play any sufficient role in the process of active species generation because the formation rate of this species is much higher in the presence of TBHP (since TBHP can also play the role of a reducing agent). Figure 1 demonstrates the stationary reaction rates, that is, the rates when the transformation of all amount of the initial complex into the active species is completed. We can assume that the correlation between the rate and the pK-value corresponds to the effect of the carboxylic acid on the catalytic activity of the 'Mn^{III}Mn$^{IV'}$ species. This effect is the result of a coordination of the acid to manganese ions and is by no means due to the reducing properties of this particular acid.

We have found that the products of the CyH oxidation are formed with participation of molecular oxygen. Indeed, when the reaction was carried out under argon atmosphere the yield of oxygenates became lower more than for 70%. The effect of O$_2$ on the yield of the products allows us to assume a radical mechanism for the CyH oxidation.

Table 1 summarizes selectivity parameters for the oxidation of various alkanes by the '**1**/TBHP/oxalic acid' system as well as (for comparison) by some other oxidizing systems. It can be seen that the selectivity parameters for the oxidations with '**1**/TBHP/oxalic acid' system (e.g. entry 1) are noticeably different from the parameters found previously for systems generating hydroxyl radicals (entries 5 and 6). However, these parameters are close to that measured for the oxidations by other systems oxidizing with participation of *tert*-butoxy radicals (entry 7). This observation allows us to propose that alkane-oxidizing species which is generated by the system under discussion is radical *tert*-BuO$^•$.

We have obtained also a kinetic evidence which supports this hypothesis. Let us analyse the mode of dependence of the maximum CyH oxidation rate on the CyH concentration shown in Fig. 5. As CyH does not form any adducts with the catalyst it is reasonable to assume that the mode of the dependence under discussion testifies the generation in the system of an oxidizing species. According to the selectivity parameters this species is *tert*-BuO$^•$. The rate of this generation is W_1:

Figure 4. UV–Vis spectra of the reaction solution in the cyclohexane oxidation catalysed by complex **1** (5×10^{-5} mol dm^{-3}) and oxalic acid (10^{-2} mol dm^{-3}). Other conditions: [TBHP]$_0$ = 0.10 mol dm^{-3}, [cyclohexane]$_0$ = 0.46 mol dm^{-3}, solvent was acetonitrile, 50 °C. Spectra were recorded at 0 (1), 30 (2) and 70 (3) min after mixing the reactants. This figure is available in colour online at www.interscience.wiley.com/journal/poc

$$TBHP \xrightarrow{cat} tert-BuO^• \qquad (1)$$

Table 1. Selectivity parameters for the alkane oxidations by various systems[a]

Entry	Alkane	Oxidizing system	Selectivity
	n-Octane		C(1):C(2):C(3):C(4)
1		TBHP–**1**–oxalic acid in MeCN; 50 °C	1.0:17.3:12.0:10.5
2		TBHP–**1**–oxalic acid in H₂O; 50 °C	1:50:47:40
3		TBHP–**1**–oxalic acid in H₂O; 50 °C[b]	1:19:21
4		H₂O₂–**1**–acetic acid in MeCN; 20 °C[c]	1.0:29:25:24
5		H₂O₂–hν in MeCN; 20 °C[d]	1.0:10.2:6.8:6.3
6		H₂O₂–Bu₄NVO₃–PCA in MeCN; 30 °C[d]	1.0:9.3:8.8:7.2
7		TBHP–Cu(MeCN)₄BF₄ in MeCN; 60 °C[e]	1:14:9:13
	2-Methylhexane		1°:2°:3°
8		TBHP–**1**–oxalic acid in MeCN; 50 °C	1.0:1.6:43
9		TBHP–**1**–oxalic acid in H₂O; 50 °C	1:32:336
10		H₂O₂–**1**–acetic acid in MeCN; 20 °C[f]	1:19:204
10		H₂O₂–hν in MeCN; 20 °C[d]	1.0:6.0:34
11		TBHP–hν in MeCN; 20 °C	1.0:5.5:18
12		H₂O₂–Bu₄NVO₃–PCA in MeCN; 30 °C[d]	1.0:5.5:24
	Isooctane		1°:2°:3°
13		TBHP–**1**–oxalic acid in MeCN; 50 °C	1.0:0.4:32
14		TBHP–**1**–oxalic acid in H₂O; 50 °C	1.0:0.6:100
15		H₂O₂–**1**–acetic acid in MeCN; 20 °C	1:16:202
16		H₂O₂–hν in MeCN; 20 °C[d]	1.0:4.0:20
17		TBHP–hν in MeCN; 20 °C	1.0:2.0:32
18		H₂O₂–Bu₄NVO₃–PCA in MeCN; 30 °C[d]	1.0:3.0:12
19		TBHP–Cu(MeCN)₄BF₄ in MeCN; 60 °C[e]	1:0:41
	Methylcyclohexane		1°:2°:3°
20		TBHP–**1**–oxalic acid in MeCN; 50 °C	1.0:0.3:0.6
21		H₂O₂–hν in MeCN; 20 °C[d]	1.0:2.0:6.0
22		H₂O₂–Bu₄NVO₃–PCA in MeCN; 30 °C[d]	1.0:3.0:5.0
	cis-1,2-Dimethylcyclohexane		*trans/cis*
23		TBHP–**1**–oxalic acid in MeCN; 50 °C	0.2
24		TBHP–**1**–oxalic acid in H₂O; 50 °C	0.6
26		H₂O₂–**1**–acetic acid in MeCN; 20 °C[c]	0.34
25		H₂O₂–hν in MeCN; 20 °C[d]	0.9
26		TBHP–hν in MeCN; 20 °C	1.0
27		H₂O₂–Bu₄NVO₃–PCA in MeCN; 30 °C[d]	0.75
	trans-1,2-Dimethylcyclohexane		*trans/cis*
28		TBHP–**1**–oxalic acid in MeCN; 50 °C	7.3
29		H₂O₂–**1**–acetic acid in MeCN; 20 °C[c]	4.1
30		H₂O₂–hν in MeCN; 20 °C[d]	1.0
31		H₂O₂–Bu₄NVO₃–PCA in MeCN; 30 °C[d]	0.8
	cis-Decalin		*trans/cis*
32		TBHP–**1**–oxalic acid in MeCN; 50 °C	0.45
33		H₂O₂–**1**–acetic acid in MeCN; 20 °C[c]	0.12
34		H₂O₂–hν in MeCN; 20 °C[d]	1.3
35		H₂O₂–Bu₄NVO₃–PCA in MeCN; 30 °C[d]	2.1

[a] All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols. Parameters C(1): C(2): C(3): C(4) are relative and normalized (i.e. calculated taking into account the number of hydrogen atoms at each carbon) reactivities of hydrogen atoms at carbons 1, 2, 3 and 4, of the chain of linear alkanes. Parameters 1°: 2°: 3° are relative and normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of branched alkanes. Parameter *trans/cis* is the ratio of *trans*- and *cis*-isomers of *tert*-alcohols formed in the oxidation of 1,2-disubstituted cyclohexanes (*cis*-DMCH, *trans*-DMCH and *cis*-decalin).
[b] *n*-Hexane was used instead of *n*-octane.
[c] For this system, refer to Reference [13a-d].
[d] These systems are believed to operate via generating hydroxyl radicals. Refer to References [14a,b,15d,f,18] *n*-Heptane was used instead of *n*-octane. In the 'H₂O₂–vanadate–PCA' reagent[14a,b,15d,f,18] PCA is pyrazine-2-carboxylic acid.
[e] For this system, refer to Reference [4].
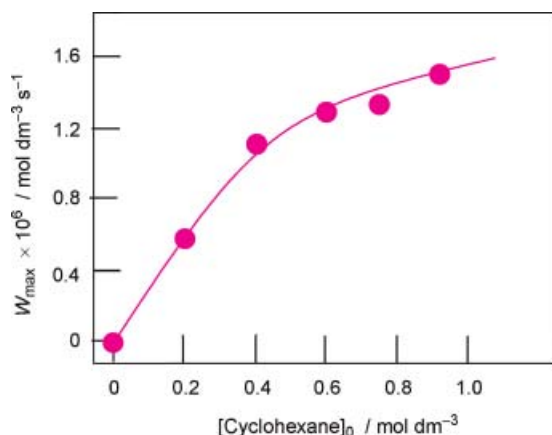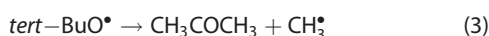[f] 2-Methylpentane was used instead of 2-methylhexane. Refer to Reference [13c].

Figure 5. Dependence of the maximum rate of the cyclohexanone + cyclohexanol accumulation in the cyclohexane oxidation catalysed by complex **1** (5×10^{-5} mol dm^{-3}) and oxalic acid (10^{-2} mol dm^{-3}) on initial concentration of cyclohexane. Conditions: $[TBHP]_0 = 0.10$ mol dm^{-3}; acetonitrile; 50 °C. This figure is available in colour online at www.interscience.wiley.com/journal/poc

Here *cat* is a catalytically active species derived from complex **1**. The oxidizing species disappears in two parallel reactions. One of these processes is the interaction between *tert*-BuO$^{\bullet}$ and CyH:

$$tert-BuO^{\bullet} + CyH \rightarrow tert-BuOH + Cy^{\bullet} \qquad (2)$$

In accordance with the literature[19] we may also consider the monomolecular decay of *tert*-butoxy radical:

$$tert-BuO^{\bullet} \rightarrow CH_3COCH_3 + CH_3^{\bullet} \qquad (3)$$

As in the presence of molecular oxygen both cyclohexyl and methyl radicals are rapidly transformed into peroxy radicals which exhibit low reactivity we can say that reactions (2) and (3) are the processes of consumption of active species. Detectable products of the CyH oxidation are formed as a result of the total rate-non-limiting subsequent stages of the cyclohexyl radical transformations.

The analysis of the kinetic scheme (1)–(3) based on an assumption that concentration of *tert*-BuO$^{\bullet}$ is quasi-stationary led to the following equation for the CyH oxidation rate:

$$-\frac{d[CyH]}{dt} = \frac{W_1}{1 + \dfrac{k_3}{k_2[CyH]}} \qquad (4)$$

The experimental data presented in Fig. 5 obey this equation because a linear dependence of the reciprocal rate of CyH oxidation on reciprocal CyH concentration is observed (Fig. 6). We can calculate parameters $W_1 = 1.7 \times 10^{-6}$ mol dm^{-3} s^{-1} and $k_3/k_2 = 0.26$ mol dm^{-3} using values for the tangent of slope of the line shown in Fig. 6 and the segment which this line cuts off on the y-axis. The value of the constant ratio k_3/k_2 agrees (with reasonable accuracy) with the value 0.19 mol dm^{-3} taken from the literature.[19] In Reference [19] parameter k_3/k_2 was obtained from the ratio of the yields of acetone and *tert*-butanol [refer to reactions (2) and 3)] during the photochemical generation of *tert*-BuO$^{\bullet}$ radicals in acetonitrile solution in the presence of CyH at the temperature of our kinetic experiments. These results are an additional support for our assumption that the *tert*-butoxy radical is the oxidizing species which operates in the catalytic system under discussion.
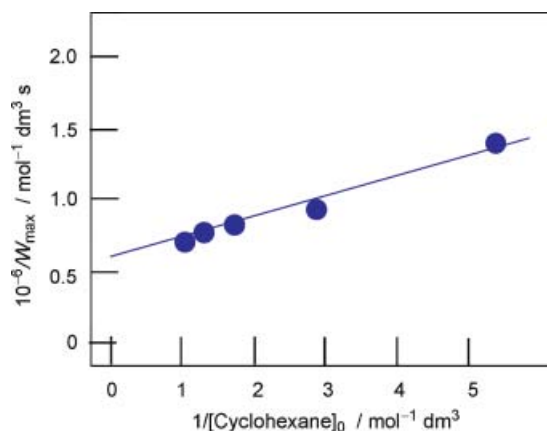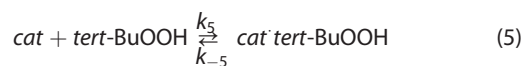

Figure 6. A linear anamorphosis of dependence $-d[CyH]/dt = f([CyH]_0)$ presented in Fig. 5. This figure is available in colour online at www.interscience.wiley.com/journal/poc

The maximum CyH oxidation rate is in direct ratio to concentration of catalyst **1** (Fig. 7). Dependence of W_{max} on initial concentration of TBHP at constant water concentration ($[H_2O] = 1.5$ mol dm^{-3}) is presented in Fig. 8. The mode of this shape allows us to assume that an intermediate adduct between TBHP and *cat* is formed. Using a simple kinetic model for the generation of active species shown below:

$$cat + tert\text{-}BuOOH \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} cat \cdot tert\text{-}BuOOH \qquad (5)$$

$$cat \cdot tert\text{-}BuOOH \xrightarrow{k_6} tert\text{-}BuO^{\bullet} \xrightarrow{CyH} \ldots \qquad (6)$$

and analysing this scheme in a quasi-equilibrium approximation we will obtain the following equation:

$$-\frac{d[CyH]}{dt} = \frac{d\Sigma[products]_i}{dt} = 0.64 k_6 \frac{K_5[TBHP][cat]}{1 + K_5[TBHP]} \qquad (7)$$
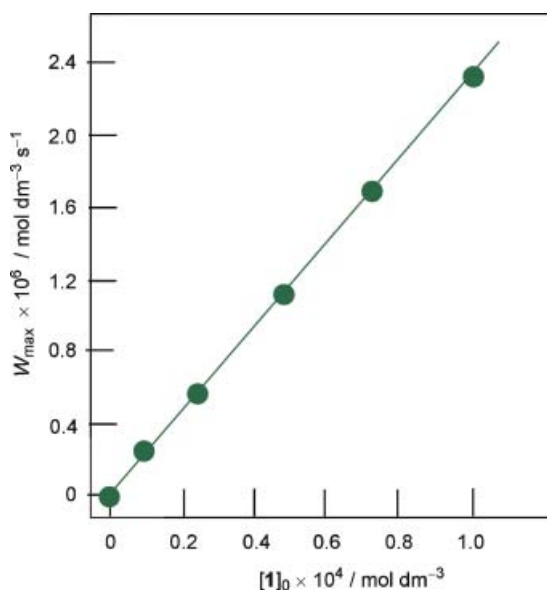

Figure 7. Dependence of the maximum rate of the cyclohexanone + cyclohexanol accumulation in the cyclohexane oxidation catalysed by complex **1** and oxalic acid (10^{-2} mol dm^{-3}) on initial concentration of **1**. Conditions: $[TBHP]_0 = 0.10$ mol dm^{-3}; $[CyH]_0 = 0.46$ mol dm^{-3}; acetonitrile; 50 °C. This figure is available in colour online at www.interscience.wiley.com/journal/poc
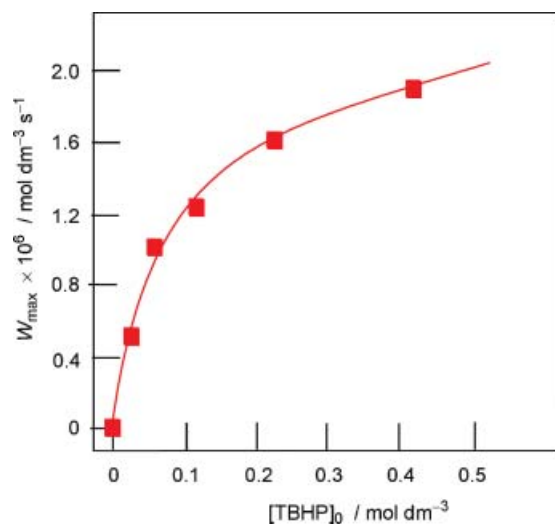
123

Figure 8. Dependence of the maximum rate of the cyclohexanone + cyclohexanol accumulation in the cyclohexane oxidation catalysed by complex **1** and oxalic acid on initial concentration of TBHP. Conditions: $[\mathbf{1}] = 5 \times 10^{-5}\,mol\,dm^{-3}$; [oxalic acid] $= 10^{-2}\,mol\,dm^{-3}$; $[CyH]_0 = 0.46\,mol\,dm^{-3}$; $[H_2O] = 1.5\,mol\,dm^{-3}$; acetonitrile; 50 °C. This figure is available in colour online at www.interscience.wiley.com/journal/poc

To simplify further analysis of the data from Fig. 8 let us transform Eqn (7) into the following one:

$$\left(-\frac{d[CyH]}{dt}\right)^{-1} = \frac{1}{0.64k_6[cat]}\left(1 + \frac{1}{K_5[TBHP]}\right) \quad (8)$$

It follows from the data of Fig. 9 (which presents the linear anamorphosis of the curve shown in Fig. 8) that the experimentally obtained parameters with reasonable accuracy correspond to the proposed model and are in the quantitative agreement with this model if we assume $K_5 = 7.4\,mol^{-1}\,dm^3$ and $k_6 = 8.4 \times 10^{-2}\,s^{-1}$. It should be noted that values K_5 and k_6 are
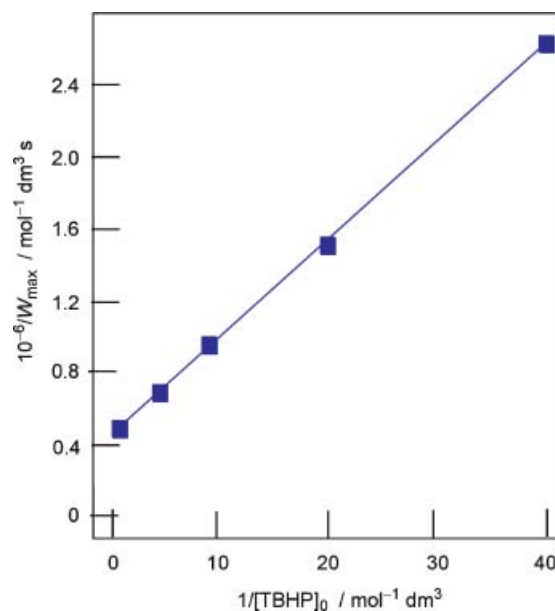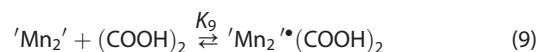

Figure 9. A linear anamorphosis of dependence $-d[CyH]/dt = f([TBHP]_0)$ presented in Fig. 8. This figure is available in colour online at www.interscience.wiley.com/journal/poc

the effective parameters because the reaction rate depends on concentrations of both water and oxalic acid. The values given above correspond to $[H_2O] = 1.5\,mol\,dm^{-3}$ and [oxalic acid] $= 10^{-2}\,mol\,dm^{-3}$.

Our data show that the reaction rate depends not only on the nature of the carboxylic acid (Fig. 1) but also on its concentration (Fig. 10). The mode of dependence of W_{max} on concentration of oxalic acid (Fig. 10) shows that an activation of the catalyst precursor **1** is possible via the formation of an adduct between **1** and oxalic acid. However, we realize that based only on the results of Fig. 10 a strict demonstration of the adduct formation is problematic since we do not know the effect of the medium acidity on the formation constant for this adduct and also on its catalytic activity. Nevertheless, we can estimate the effective equilibrium constant at fixed [TBHP] assuming that the formation of an adduct between initial manganese compound and oxalic acid leads to the activation of the catalyst. Let us denote all dimeric species containing manganese ions as 'Mn$_2$' including to this formula intermediates which both contain and do not contain TBHP but do not contain oxalic acid (the concentrations of such species are controlled by the corresponding equilibrium constants for the formation of peroxo complexes). In this case, we can denote as 'Mn$_2$''(COOH)$_2$ all adducts between dinuclear manganese species and oxalic acid. We will come to equation:

$$'Mn_2' + (COOH)_2 \underset{}{\overset{K_9}{\rightleftarrows}} 'Mn_2'^{\bullet}(COOH)_2 \quad (9)$$

Constant of this equilibrium K_9 is the effective parameter which depends on concentrations of TBHP, water as well as on the acidity of the reaction medium. In the half-effect point ['Mn$_2$'] = ['Mn$_2$''(COOH)$_2$], that is, $K_9[(COOH)_2] = 1$ because oxalic acid is present in a great excess over catalyst precursor **1**. It follows from data of Fig. 10 that at [TBHP] $= 0.1\,mol\,dm^{-3}$ and $[H_2O] = 1.5\,mol\,dm^{-3}$ the half-effect is attained at $[(COOH)_2] \approx 10^{-3}\,mol\,dm^{-3}$ and, consequently, $K_9 \approx 10^3\,mol^{-1}\,dm^3$.
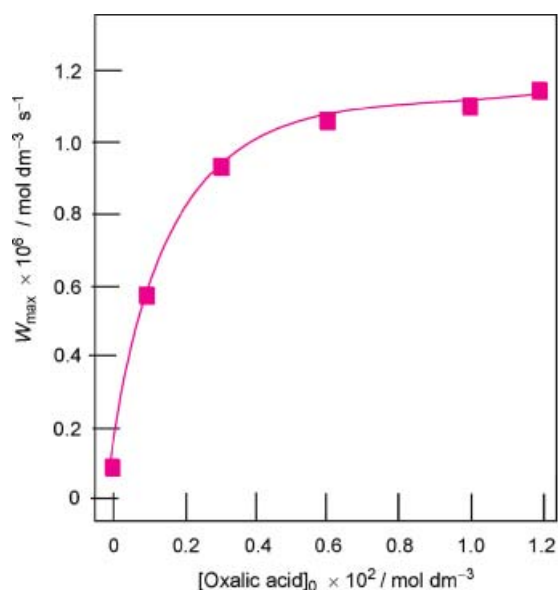

Figure 10. Dependence of the maximum rate of the cyclohexanone + cyclohexanol accumulation in the cyclohexane oxidation catalysed by complex **1** and oxalic acid on concentration of oxalic acid. Conditions: $[\mathbf{1}] = 5 \times 10^{-5}\,mol\,dm^{-3}$; $[CyH]_0 = 0.46\,mol\,dm^{-3}$; $[TBHP]_0 = 0.10\,mol\,dm^{-3}$; acetonitrile; 50 °C. This figure is available in colour online at www.interscience.wiley.com/journal/poc
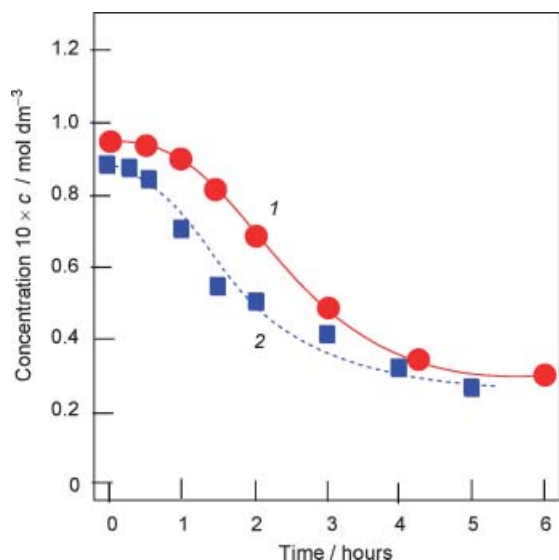
Figure 11. Kinetic curves of TBHP consumption under the action of **1** and oxalic acid in the presence (curve 1) and in the absence (curve 2) of cyclohexane. Conditions: $[1] = 5 \times 10^{-5}\,mol\,dm^{-3}$; [oxalic acid] $= 10^{-2}\,mol\,dm^{-3}$; $[CyH]_0 = 0.46\,mol\,dm^{-3}$; $[TBHP]_0 = 0.10\,mol\,dm^{-3}$; 50 °C.

We have demonstrated that the rate of the TBHP decomposition in the presence and in the absence of CyH is practically the same (Fig. 11) and that this rate is a few times higher than the CyH oxygenation rate (Fig. 12). As the CyH oxidation is induced by *tert*-butoxy radicals (see above) the rate of its transformation into oxygenates at $[CyH] \rightarrow \infty$ is equal to the rate of generation of *tert*-BuO• radicals in the catalysed TBHP decomposition. Addition of CyH to the reaction solution does not affect the TBHP decomposition rate, and this allows us to reject a chain-radical mechanism for the decomposition process with participation of *tert*-butoxy radicals. We assume on this basis that the main route
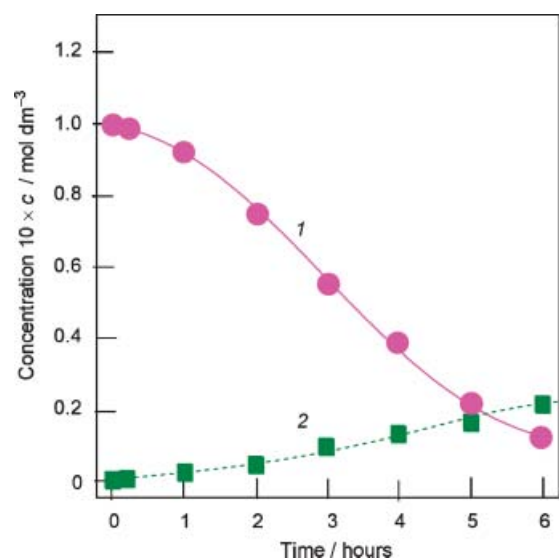
of the catalysed TBHP decomposition is its molecular decay. Another process – with generation of *tert*-BuO• radicals – is only a minor route. The rate ratio for these two routes of the catalytic TBHP transformation is close to 10. It explains why the system uses only *ca* 10% of TBHP for the CyH oxygenation whereas 90% decomposes non-productively.

EXPERIMENTAL

Complex **1** was synthesized as described in Reference [17]. The oxidations of hydrocarbons were carried out in acetonitrile in air in thermostated (25 °C) Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 2 ml. Initially, a portion of TBHP (70% aqueous) was added to a solution of the catalyst **1**, co-catalyst (typically oxalic acid) and CyH. After certain time intervals samples (about 0.2 ml) were taken. To determine the concentration of a sum of the stable CyH oxidation products (cyclohexanone and cyclohexanol) the sample of the reaction solution was typically treated with PPh₃ (for this method, refer to References [14a,b,15]) and analysed by GC (LKhM-80-6 instrument, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas was argon). Other saturated hydrocarbons were oxidized under analogous conditions. Concentration of TBHP was measured by titration of the reaction mixture aliquots with 0.1 mol dm⁻³ NaI in acetic anhydride (control by UV–Vis spectroscopy).

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Figure 12. Kinetics of TBHP consumption (curve 1) and cyclohexanone + cyclohexanol accumulation (curve 2) in the cyclohexane oxidation. Conditions: $[1] = 5 \times 10^{-5}\,mol\,dm^{-3}$; [oxalic acid] $= 10^{-2}\,mol\,dm^{-3}$; $[CyH]_0 = 0.92\,mol\,dm^{-3}$; $[TBHP]_0 = 0.10\,mol\,dm^{-3}$; 50 °C.

125

J. Phys. Org. Chem. **2008**, 21 119–126

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126