Tetrahedron 68 (2012) 8589-8599

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet



Hydrocarbon oxygenation with Oxone catalyzed by complex $[Mn_2L_2O_3]^{2+}$ (L=1,4,7-trimethyl-1,4,7-triazacyclononane) and oxalic acid

Georgiy B. Shul'pin^{a,*}, Yuriy N. Kozlov^a, Lidia S. Shul'pina^b, Armando J.L. Pombeiro^c

^a Semenov Institute of Chemical Physics, Russian Academy of Sciences, ulitsa Kosygina, dom 4, Moscow 119991, Russia

^b Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ulitsa Vavilova, dom 28, Moscow 119991, Russia

^c Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049–001, Lisbon, Portugal

ARTICLE INFO

Article history: Received 14 March 2012 Received in revised form 13 July 2012 Accepted 31 July 2012 Available online 7 August 2012

Keywords: Alkanes Benzene C–H activation Manganese complexes Oxygenation Peroxysulfate

ABSTRACT

Oxone (peroxysulphate) very efficiently oxidizes benzene to *p*-quinone (TON 1140) and alkanes to the corresponding alcohols and ketones (aldehydes) in aqueous acetonitrile 50 °C if catalytic amounts of complex $[Mn_2L_2O_3]^{2+}$ (L=1,4,7-trimethyl-1,4,7-triazacyclononane) and oxalic acid are present in the solution. In contrast to the similar reaction with H₂O₂, the alkane oxidation with Oxone does not afford the corresponding alkyl hydroperoxides. Phenol was quantitatively oxidized to a mixture of *p*-quinone and pyrocatechol (9:1 ratio). Cyclohexanol gave cyclohexanone (TON 400). The proposed mechanism includes the formation of an oxidizing species containing the Mn(V)=O fragment. A kinetic study demonstrated that an *adduct* of $[Mn_2L_2O_3]^{2+}$ and oxalic acid is formed in the initial stage. This *adduct* reacts with Oxone to generate the oxidizing species.

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1. Introduction

Peroxidic compounds, especially 'green' hydrogen peroxide and peroxysulfates, are very efficient oxidizing reagents widely used in organic synthesis in the presence of metal catalysts.¹ Potassium peroxymonosulfate (KHSO₅) mainly used in the form of Oxone[®] (2KHSO₅·KHSO₄·K₂SO₄) easily oxidizes² sp³-C–H compounds,³ aromatic hydrocarbons,⁴ olefins,⁵ alcohols,⁶ and phenols.⁷ Dimanganese fragments in combination with Oxone were used for remote regioselective catalytic oxygenation of alkyl groups in the Brudvig-Crabtree molecular recognition systems.⁸ Soluble and solid derivatives of transition metals catalyze degradation of dyes under the action of Oxone.⁹ A dinuclear Mn(III)/Mn(IV) complexes in combination with Oxone provide functional model systems for the oxygen-evolving complex of photosystem II.¹⁰ A dinuclear complex of Mn(II) with 2,6-pyridinedicarboxylate acts as an oxygen evolving complex with Oxone.¹¹

The dinuclear manganese(IV) complex $[LMn(O)_3MnL](PF_6)_2$ (complex **1**; L is 1,4,7-trimethyl-1,4,7-triazacyclononane,

TMTACN) has been synthesized and characterized by Wieghardt and co-workers.¹² This compound is known to catalyze some oxidations of organic compounds, such as olefins and phenols with hydrogen peroxide.¹³ Previously it has been found¹⁴ that complex **1** catalyzes the oxidations by hydrogen peroxide in acetonitrile solution much more efficiently if a small amount of a carboxylic acid is added to the reaction solution. It has been demonstrated that the '1/carboxylic acid/H₂O₂' combination very efficiently oxidizes inert alkanes^{14,15} to afford mainly the corresponding alkyl hydroperoxides, which are transformed further into the more stable ketones, aldehydes, and alcohols. The system oxidizes not only alkanes but also epoxidizes olefins,^{15a,f,16} transforms alcohols into ketones, (aldehydes),^{15a,f,17} and sulfides into sulfoxides.^{15a} The reaction with olefins afforded the products of dihydroxylation^{16a} in addition to the corresponding epoxides. Catalyst 1 was used in combination with oxalic acid in a study devoted to the decoloration of dye Rhodamine 6G.^{16c} Recently Veghini, Fischer and their co-workers¹⁸ prepared the insoluble salt of formula $[LMn(\mu-O)_3MnL]_2[SiW_{12}O_{40}]$, which is active as a catalyst in the oxidation of alcohols and olefins in the presence of carboxylic acids. Alkanes and olefins can be oxidized by tertbutyl hydroperoxide^{15a,19} using complex **1** as a catalyst. The reaction is also significantly accelerated by the presence of a small amount of a carboxylic acid.

^{*} Corresponding author. Tel.: +7 495 9397317; fax: +7 495 6512191; e-mail addresses: Shulpin@chph.ras.ru, gbsh@mail.ru (G.B. Shul'pin).

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Continuing the studies of oxidations catalyzed by the '1/carboxylic acid' combination we decided to explore the possibility of replacing hydrogen peroxide with Oxone. It is interesting to compare the mechanisms of oxidations of the two oxidants. Moreover, previously we were unsuccessful in our attempts to oxidize benzene to phenol and/or quinone in substantial yields using H_2O_2 . Due to this, it was important to attempt the usage of Oxone for this purpose. In the present work, we have studied for the first time the oxidation of benzene and various alkanes with Oxone catalyzed by complex **1** in the presence of a small amount of oxalic acid. We have found that oxalic acid is an essential component of the catalytic system.

2. Results and discussion

2.1. Oxidation of benzene

We found that the '1/oxalic acid (2)/Oxone (3)' system efficiently oxidizes benzene (compound 4) to *p*-quinone (7) in aqueous acetonitrile (Scheme 1). The amount of compound 7 attained 0.25 mol when one mol of **3** was used. Turnover numbers (TONs) were up to 1140 based on compound **1** as a catalyst. Fig. 1 shows some examples of the kinetic curves of the reactions carried out at different concentrations of **1**. The conditions are given in the caption. At low concentrations of **1** ($<1.0\times10^{-5}$ M) the mode of kinetic accumulation curves (A and B) typical for the reaction with auto-acceleration can be clearly seen. It can be also noticed that at relatively high concentrations of **1** the kinetic curves (C and D) have maxima because the formed *p*-quinone is over-oxidized with Oxone. The induction period (Fig. 2, curve A) is substantially diminished (curve C)

if some amount of hydroquinone (**6**) is added to the reaction mixture. Fig. 2, curve D demonstrates that **6** is rapidly oxidized to *p*quinone and over-oxidized by the same system. It is known that *p*alkoxyphenols are easily oxidized to *p*-quinone with Oxone in acetonitrile—water (2:1) even in the absence of a metal catalyst.²⁰ We have found that phenol is very rapidly oxidized by the '**1**/ oxalic acid/Oxone' system: the reaction of phenol (0.03 M) with catalyst **1** (3.0×10^{-5} M), oxalic acid (0.05 M) and Oxone (0.032 M) in aqueous acetonitrile at 50 °C gave after 5 min in quantitative yield *p*-quinone (0.027 M) and pyrocatechol (0.003 M). Thus, it is reasonable to assume that *p*-quinone is the final product formed via the consecutive oxidation of phenol and hydroquinone.

We have studied the kinetics of benzene oxidation by the 'Oxone/1/oxalic acid' system in aqueous acetonitrile. As the process occurs with an auto-acceleration we measured maximum initial rates W_0 (as an example, see: slope of a dotted line A' in Fig. 1) of the reaction in the initial period. The lag periods in the kinetic curves are much shorter if relatively high concentrations of 1 are used (compare curves A and D in Fig. 1). Figs. 3–6 present the dependences of rates W_0 on initial concentrations of the reactants 1, 4, 3, and 2, respectively. In the cases of the first three reactants these dependences at their relatively low concentrations are linear.

The dependence of the maximum reaction rate W_0 on the concentration of oxalic acid (**2**) (Fig. 6A), as well as dependences shown in Figs. 3–5, allow us to assume that an *adduct* is formed in the initial stage. This *adduct* reacts with Oxone to generate the species X, which induces the substrate oxidation:

$$\mathbf{1}' + \mathbf{2} \rightleftharpoons adduct \quad (\text{constant } K_1) \tag{1}$$

$$adduct + \mathbf{3} \rightleftharpoons X$$
 (constant K'_1) (1')

$$X + \mathbf{4} \rightarrow \text{products} \quad (\text{constant } k_2)$$
 (2)

Here species $\mathbf{1}'$ is an active form of the catalyst, which is produced during the lag period. Stage (2) is the rate limiting one in the sequence of transformations associated to the substrate oxidation. We can write for the initial reaction rate:

$$W_0 = -d[4]/dt = k_2[X][4]_0 \tag{3}$$



Scheme 1. Oxidation of benzene.



Fig. 1. Accumulation of *p*-quinone (**7**) in the oxidation of benzene (**4**; initial concentration 0.1 M) with Oxone (**3**; initial concentration.0.032 M) catalyzed by complex **1** and oxalic acid (**2**; 0.05 M) at different concentrations of **1**: 0.5×10^{-5} (curve A; TON was 1140 after 10 h; the maximum initial rate W_0 was determined from the slop of a dotted straight line A'), 1.0×10^{-5} (curve B), 10×10^{-5} (curve C) and 20×10^{-5} M (curve D; yield after 2.5 h was 0.25 mol of **7** per 1 mol of Oxone). Solvent was MeCN–D₂O (2:1 v/v), temperature 50 °C, total volume of the reaction solution was 5 mL.



Fig. 2. Accumulation of *p*-quinone (**7**) in the oxidation of benzene (**4**; 0.1 M) (curves A, B and C) with Oxone (**3**; initial concentration 0.032 M) catalyzed by complex **1** (5.0×10^{-5} M) and oxalic acid (**2**; 0.05 M) (curve A). Curve B: the same with addition of hydroquinone (**6**; 1.0×10^{-3} M). Curve C: the parameters of curve B after subtraction of 1.0×10^{-3} M (i.e., initial concentration of added hydroquinone). Curve D: accumulation of *p*-quinone (**7**) in the oxidation of hydroquinone (**6**; 0.1 M) under the same conditions. Solvent was MeCN–D₂O (2:1 *v*/*v*), temperature 50 °C, total volume of the reaction solution was 5 mL.

The concentration X in the quasi-equilibrium approximation taking into account that [X] << [adduct] and concentration [adduct] is comparable with $[1]_0$ can be calculated using the following equation:



Fig. 3. Dependence of the maximum initial rate W_0 (an example of measuring W_0 is shown for curve A in Fig. 1: the rate was determined from the slop of a dotted straight line A') of the accumulation of *p*-quinone (**7**) in the oxidation of benzene (0.1 M) with Oxone (initial concentration .032 M) catalyzed by complex **1** and oxalic acid (0.05 M) on concentration of **1**. Solvent was MeCN–D₂O (2:1 v/v), total volume 5 mL, temperature 50 °C.



Fig. 4. Dependence of the maximum initial rate W_0 of the accumulation of *p*-quinone (7) in the oxidation of benzene (4) with Oxone (initial concentration .032 M) catalyzed by complex 1 (5.0×10^{-5} M) and oxalic acid (0.05 M) on initial concentration of benzene. Solvent was MeCN–D₂O (2:1 ν/ν), total volume 5 mL, temperature 50 °C.

$$[X] = \frac{K_1' K_1 [\mathbf{1}']_0 [\mathbf{2}]_0 [\mathbf{3}]_0}{1 + K_1 [\mathbf{2}]_0}$$
(4)

In this case we can expect the linear dependence of the reciprocal of the reaction rate on the reciprocal of $[2]_0$:

$$\frac{1}{W_0} = \frac{1}{k_2 K_1' K_1 [\mathbf{1}']_0 [\mathbf{3}]_0 [\mathbf{4}]_0} \left\{ \frac{1}{[\mathbf{2}]_0} + K_1 \right\}$$
(5)

The analysis of the experimental dependence of W_0 on $[2]_0$ (Fig. 6A) using the least-squares procedure and coordinates, which correspond to the linear dependence $1/W_0$ on $1/[2]_0$ (equation (5)) led to the following result for the experimental conditions of Fig. 6A:



Fig. 5. Dependence of the maximum initial rate W_0 of the accumulation of *p*-quinone (**7**) in the oxidation of benzene (initial concentration 0.1 M) with Oxone (**3**) catalyzed by complex **1** (5.0×10^{-5} M) and oxalic acid (0.05 M) on initial concentration of Oxone. Solvent was MeCN–D₂O (2:1 ν/ν), total volume 5 mL, temperature 50 °C.



Fig. 6. Dependence of the maximum rate W_0 of the accumulation of *p*-quinone (**7**) in the oxidation of benzene (0.1 M) (curve A) with Oxone (initial concentration.0.032 M) catalyzed by complex **1** (5.0×10^{-5} M) and added oxalic acid on its concentration. Dashed curve B: simulated curve calculated in accordance with equation (7). Curve C: the linearization of the dependences presented by curve A in coordinates $1/W_0-1/$ [oxalic acid]₀. Curve D: the dependences presented by line C in expanded (including one more point) scale. Solvent was MeCN–D₂O (2:1 v/v), total volume 5 mL, temperature 50 °C.

$$\frac{1}{k_2 K_1' K_1[\mathbf{1}']_0[\mathbf{3}]_0[\mathbf{4}]_0} = 980 \text{ s and}$$
(6')

$$\frac{1}{k_2 K_1' [\mathbf{1}']_0 [\mathbf{3}]_0 [\mathbf{4}]_0} = 1.75 \times 10^5 \text{ M}^{-1} \text{ s}$$
 (6")

It follows from equations (6') and (6'') that K_1 =180 M⁻¹, that is, for the conditions of Fig. 6A we have:

$$1/W_0 = 980/[\mathbf{2}]_0 \ 1.75 \times 10^5 \ \mathrm{M}^{-1} \ \mathrm{s}$$
 (7)

A close coincidence of the experimental curve A and simulated curve B in Fig. 6 indicates that equation (5) satisfactorily describes the experimental data. Therefore, the consequence of stages (1)-(2) is in good agreement with the real mechanism of the reaction.

The oxidation of benzene in the absence of oxalic acid occurs with a very long lag period and is very slow. Thus, under the conditions of the experiment shown in Fig. 1C at $[2]_0=0$ M, the concentration of *p*-quinone after 2 h was 0 M and only after 6 h [7] attained 0.002 M, whereas in the presence $[2]_0=0.05$ M this concentration was 0.007 M after 2 h. It is important to emphasize that other carboxylic acids do not remove the lag period and do not accelerate the benzene oxidation. We have found that under the conditions of Fig. 1C, if acetic or trifluoroacetic acid (0.1 M) are added, no *p*-quinone (7) was detected in the reaction mixture after 2 h. Only after 5 h, [7] attained 0.0035 and 0.005 M for the cases of CH₃COOH and CF₃COOH, respectively.

2.2. Oxidation of cyclic, linear, and brunched alkanes

The efficiency of methylene group oxidation in arylalkanes (Fig. 7) is comparable with the oxygenation of benzene (Fig. 1, curve D). Methylene groups in ethylbenzene are activated by the neighboring phenyl ring and due to this ethylbenzene is more reactive than cyclohexane (Fig. 8). To check whether alkyl hydroperoxides are formed in this reaction we compared the chromatograms of the reaction mixtures obtained before and after the reduction of the solution with an excess of triphenylphosphine (for this convenient and simple method developed previously by one of us, see Refs. 21). If an excess of solid PPh₃ is added to a sample of the reaction solution, ca. 10 min before GC analysis, the alkyl hydroperoxide, ROOH, present in the reaction mixture 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 the alcohol, ketone, and alkyl hydroperoxide present in the reaction solution.²¹ In the present study we have found for the oxidations of ethylbenzene and cyclohexane that there is practically no difference between chromatograms obtained for the untreated solution and the same sample reduced with PPh₃. It means that alkyl hydroperoxides are present in negligible amounts and the reaction gives predominantly the alcohol and ketone. The alcohol is easily oxidized by the catalytic system to the corresponding ketone, which has been demonstrated in a special experiment. Heating a biphasic solution of complex **1** (0.0005 mmol) and oxalic acid (0.01 mmol), cyclohexanol (0.48 mmol), and Oxone (0.49 mmol) in air in a mixture of MeCN (2 mL) and H₂O (1.4 mL) at 70 °C gave after 2 h cyclohexanone (0.20 mmol; yield 42%; TON 400).

Tables 1 (see also Section S1 and Figs. S1–S3) and 2 demonstrate that parameters of regio-, bond-, and stereo-selectivity for



Fig. 7. Accumulation of acetophenone and 1-phenylethanol in the oxidation of ethylbenzene (initial concentration 0.16 M) with Oxone (initial concentration 0.013 M) catalyzed by complex **1** (5.0×10^{-4} M) and oxalic acid (0.05 M). Solvent: a mixture of acetonitrile (2.9 mL) and water (2.0 mL). 50 °C.



Fig. 8. Accumulation of cyclohexanone and cyclohexanol in the oxidation of cyclohexane (initial concentration 0.17 M) with Oxone (initial concentration 0.013 M) catalyzed by complex **1** (5.0×10^{-4} M) and oxalic acid (0.05 M). Solvent: a mixture of acetonitrile (2.9 mL) and water (2.0 mL). 50 °C.

the oxidations of certain alkanes by the '1/oxalic acid/Oxone' (Table 2, Entry 1) system are substantially higher than the corresponding parameters measured for the systems, which oxidize with the participation of hydroxyl radicals (Table 2, Entries 5–17)

or tert-butoxy radicals (Table 2, Entries 19 and 20). The high selectivity parameters in the oxidation catalyzed by complex $[0 \subset Cu_4[N(CH_2CH_2O)_3]_4(BOH)_4][BF_4]_2$ (13) suggest there is substantial steric hindrance in the reaction center, and it is possible to assume that the reaction proceeds in a cleft.^{26b} Very large steric hindrance was noticed for the oxidations with H₂O₂ catalyzed by complex **8** (Table 2, Entry 4)^{15e} and titanosilicate TS-1 where the reaction proceeds in nano channels (Table 2, Entry 22).^{26f} The profile of the peaks in chromatogram of hydroxylated methylcyclohexanes for the catalytic oxidation by the '1/oxalic acid/ Oxone' system (Fig. S2a) is similar with the profile for the oxidation with the participation of small hydroxyl radicals (Fig. S2b). It can be clearly seen that in the oxidations catalyzed by the sterically hindered complexes 13 and 14 (Tables 1 and 2, Entries 18 and 19; Fig. S2c and d) isomers P6 and P7 are formed in relatively small amounts. Another very interesting peculiarity of the 1/oxalic acid/Oxone system is the inversion of configuration in the oxidation of trans-1,2-dimethylcyclohexane: the trans/cis ratio of isomers of tert-alcohols with mutual trans- and cis-orientation of the methyl groups is only 0.2 (Table 2, Entry 1). The same phenomenon has been found by us previously for the oxidations of *trans*-1,2-dimethylcyclohexane with TBHP catalyzed by copper complexes bearing voluminous ligands (Table 2, Entries 18 and 19). Thus, based on selectivity studies of the oxidations by the '1/oxalic acid/Oxone' system, we can conclude that the bulky methylated azacyclononane ligands surrounding the manganese active reaction centers in 1 sterically hinder the approach of certain fragments of hydrocarbon molecules.

2.3. On the possible mechanism of the hydrocarbon oxygenation with the '1/oxalic acid/Oxone' system

Previously, on the basis of kinetic peculiarities of the oxidations of alkanes^{27a} and olefins^{16a} by the '**1**/carboxylic acid/H₂O₂' system, catalytic cycles for these processes have been proposed. The interaction of complex **1** with a carboxylic acid and one molecule of hydrogen peroxide leads to the formation of a catalytically active species **Cat** (see Scheme S1). Carboxylic acid and the corresponding carboxylate fragment play the roles of proton transfer reagents. Hydrogen peroxide reduces one of Mn(IV) ions in the binuclear compound **1** to Mn(III). The details of this catalytic oxidation are given in Supplementary data, Section S2. This process is similar to the first step of the catalytic cycle proposed for the oxidations by the 'vanadium derivative/pyrazine-2-carboxylic acid (PCA)/H₂O₂' reagent^{23,27b} and the 'vanadate/acid' system,²⁴ where V(V) ion is reduced by H₂O₂ to V(IV).

In the present work we found that the oxidation with Oxone exhibits some features that are similar to feature previously found by us for the oxidation with hydrogen peroxide. However, some other properties demonstrate that the two systems are

Table 1

Accumulation of oxygenat	tes (see also Fig. S1) in	the oxidation of methylc	yclohexane (MCH) with	Oxone catalyzed by 1 and	l oxalic acid
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Time (min)	Products (concentration, mM) ^b											1°	2°	3° [℃]	
	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12			
60	0.04	0.15	0.14	0.13	0.45	0.04	0.08	0.06	0.03	0.09	0.05	0.009	1	12	150
90	0.06	0.33	0.34	0.30	1.00	0.08	0.16	0.14	0.07	0.18	0.09	0.06	1	12	167
120	0.06	0.55	0.66	0.59	1.77	0.13	0.29	0.23	0.11	0.28	0.14	0.045	1	11	161
180	0.07	0.75	1.40	1.10	3.10	0.14	0.40	0.20	0.10	0.41	0.20	0.07	1	6	135

^a Reaction conditions: [1]₀=5×10⁻⁴ M; [oxalic acid]₀=5×10⁻² M; [Oxone]₀=0.013 M; [MCH]₀=0.13 M; MeCN (2.9 mL); H₂O (2.0 mL); 50 °C.

^b Concentrations of isomers (after reduction with PPh₃) are given. Oxygenate products: **P1**: cyclohexanecarboxaldehyde, **P2**: 2-methylcyclohexanone, **P3**: 3-methylcyclohexanone, **P4**: 4-methylcyclohexanone, **P5**: 1-methylcyclohexanol, **P6**: *trans*-2-methylcyclohexanol, **P7**: *cis*-2-methylcyclohexanol, **P8**: *trans*-3-methylcyclohexanol, **P9**: *trans*-4-methylcyclohexanol, **P1**: *cis*-4-methylcyclohexanol, **P1**2: cyclohexylmethanol. Typical chromatogram of the reaction mixture is shown in Fig. S2a. Molecular formulas of oxidation products **P1**–**P12** are given in Fig. S3.

^c Bond selectivity, i.e., relative normalized reactivities (using concentrations of isomeric alcohols) of hydrogen atoms at primary (1°), secondary (2°) and tertiary (3°) carbon atoms of MCH determined after reduction with PPh₃.

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Selectivity parameters in oxidations of alkanes by	y certain catalytic systems ^a
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Entry	Catalytic system	C(1):C(2):C(3):C(4)	1°:2°:3°	trans/cis			
		n-Heptane	МСН	cis-1,2-DMCH	trans-1,2-DMCH		
1	1/oxalic acid/Oxone (this work)	1:30:28:30	1:12:150	0.5	0.2		
2	1 /acetic acid/H ₂ O ₂ (Ref. 14a)	1:46:35:34	1:26:200	0.34	4.1		
3	1/oxalic acid/TBHP (Ref. 22a)	1:14:13:12	1:0.4:32	0.2	7.3		
4	8 /oxalic acid/H ₂ O ₂ (Ref. 15e) ^b	1:91:99:68		0.31	13		
5	FeSO ₄ /H ₂ O ₂ (Ref. 22b)	1:5:5:4.5	1:3:6	1.3	1.2		
6	hv/H ₂ O ₂ (Ref. 22b)	1:7:6:7		0.9			
7	Fe(ClO ₄) ₃ /H ₂ O ₂ (Ref. 22b)	1:9:9 (with <i>n</i> -hexane)	1:7:43				
8	9 /PCA/H ₂ O ₂ (Ref. 22c) ^c	1:6:6:5		3.5	5.1		
9	10 /H ₂ O ₂ (Ref. 22d) ^d	1:10:10:6		1.6	1.2		
10	11 /H ₂ O ₂ (Ref. 22d) ^e	1:15:14:11		0.9	1.3		
11	VO ₃ ⁻ PCA-H ₂ O ₂ (Ref. 23)	1:9:7:7	1:6:18	0.75	0.8		
12	VO ₃ ⁻ /H ₂ SO ₄ /H ₂ O ₂ (Ref. 24)	1:7:7:6		0.86	0.9		
13	Cp* ₂ Os/py/H ₂ O ₂ (Ref. 25a)	1:7:7:7	1:8:23	1.0	0.9		
14	Os ₃ (CO) ₁₂ /py/H ₂ O ₂ (Ref. 21c)	1:4:4:4	1:5:11	0.85			
15	12 /H ₂ O ₂ (Ref. 25b) ^f	1:5.5:5.0:4.6	1:4:10	0.9			
16	OsCl ₃ /H ₂ O ₂ (Ref. 25c)	1:12:10:3.5					
17	13 /CF ₃ COOH/H ₂ O ₂ (Ref. 26a) ^g	1:8.4:6.7:5.3	1:5:14	0.8	0.8		
18	13 /TBHP (Ref. 26b) ^g	1:34:23:21	1:16:128	0.4	0.1		
19	14 /TBHP (Ref. 26c) ^h	1:10:8:11	1:15:170	0.6	0.1		
20	Cu(MeCN) ₄ ⁺ /TBHP (Ref. 26d)	1:14:9:13					
21	Ti-MMM-2/H ₂ O ₂ (Ref. 26e)	1:9:7:6.5	1:6:113	0.9	0.9		
22	TS-1/H ₂ O ₂ (Ref. 26f)	1:80:193:100	No products	No products	No products		

^a Regioselectivity parameter C(1):C(2):C(3):C(4) is the relative normalized (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 n-heptane. Bond selectivity parameter 1°: 2°: 3° is the relative normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of methylcyclohexane. Stereoselectivity parameter trans/cis is the ratio of isomers of tert-alcohols with mutual trans- and cis-orientation of the methyl groups formed in the oxidation of cis- and trans-1,2-dimethylcyclohexane (DMCH). All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols. ^b Compound **8** is complex $[Mn_2(R-L^{Me2R})_2(\mu-O)_2]^{3+}$ where $R-L^{Me2R}$ is (R)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane.

^c Compound **9** is $[Fe_2(hptb)(\mu-OH)(NO_3)_2]^{2+}$ where hptb is *N,N*/*N*-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane.

^d Compound **10** is $[Fe_2(N_3O-L)_2(\mu-O)(\mu-OOCCH_3)]^+$ where L is 1-carboxymethyl-4,7-dimethyl-1,4,7-triazacyclononane.

Compound **11** is $[Fe_4(N_3O_2-L)_4(\mu-O)_2]^{4+}$ where L is 1-carboxymethyl-4,7-dimethyl-1,4,7-triazacyclononane.

^f Compound **12** is (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium.

Compound **13** is $[0 \subset Cu_4 \{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$.

^h Compound **14** is Cu(H₃L)(NCS) where H₄L is N, N, N', N'-tetrakis(2-hydroxyethyl)ethylenediamine.

different. Thus, the oxidation with the '1/Oxone' combination in the presence of other carboxylic acids (acetic or trifluoroacetic) proceeds with a very long lag period; the alkane oxidation with the '1/oxalic acid/Oxone' system affords alcohols and ketones whereas the '1/oxalic acid/H₂O₂' system generates primarily alkyl hydroperoxides. Oxone hydroxylates trans-1,2-dimethylcyclo hexane with partial inversion of configuration whereas hydrogen peroxide hydroperoxidizes this isomer with partial retention of configuration. The reactions with both oxidizing reagents exhibit a lag period and auto-acceleration in the beginning of the processes.

On the basis of obtained kinetic and selectivity data, as well as on the information from the literature, 2^{28-32} we propose for the oxidation by the '1/oxalic acid/Oxone' system the mechanism shown in Scheme S2. We assume that the reaction proceeds via the catalytically active species Cat, which is formed during the lag period. Species **Cat** is the same one as $\mathbf{1}'$ in equation (1). Species **Cat** reacts with Oxone to produce the dinuclear [Mn(V)=OMn(IV)- $\mathrm{OH}|^{2+}$ complex, which interacts further with the hydrocarbon abstracting the hydrogen atom from the alkane to form the alkyl radical, Alk•. Alkyl radicals, Alk•, can in part react with molecular oxygen present in the solution. The partial inversion of configuration is due to this reaction. This mechanism is described in more detail in Section S2. It is necessary to emphasize that an alkyl peroxyl radical, AlkOO•, formed in this route is unable to initiate the radical-chain oxidation³³ of cyclohexane or other relatively inert C-H compounds because in our case the whole process is carried out under very mild conditions (in solution at low temperature).^{33c,d} Our kinetic calculations presented in Appendix support this conclusion.

3. Conclusion

The '1/oxalic acid/Oxone' system described in this paper for the first time very efficiently oxidizes benzene, phenol and hydroquinone to p-quinone, alkanes to alcohols and ketones, and alcohols to ketones. The proposed mechanism includes the formation of an oxidizing species containing the Mn(V)=O fragment. An adduct of $[Mn_2L_2O_3]^{2+}$ and oxalic acid is formed in the initial stage. This *ad*duct reacts with Oxone to generate the oxidizing species.

4. Experimental section

The catalyst 1 and co-catalyst 2 were used in the form of a stock solution. Aliquots of these solutions were added to the reaction mixtures in hydrocarbon oxidations. The reactions were typically carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring and using aqueous MeCN as solvent (the volumes of water and acetonitrile are given in the captions to the Figs.). Precatalyst 1 was introduced into the reaction mixture in the form of a stock solution in acetonitrile. The substrate (benzene or alkane) was then added and the reaction started when solid Oxone was introduced in one portion. (CAUTION. The combination of air or molecular oxygen and Oxone with organic compounds at elevated temperatures may be explosive!). After certain time intervals a solution of 1,4-dinitrobenzene in acetone was added to the samples at room temperature (all sodium salts including unreacted Oxone were precipitated during this procedure). Concentrations of products were measured using a ¹H NMR method (D₂O was used as a component of the solvent; 'Bruker AMX-400' instrument, 400 MHz). For the determination of concentrations of substrates

and products, the corresponding signals were integrated using added 1,4-dinitrobenzene as an internal standard. The reactions of alkanes were stopped by cooling, and analyzed twice, i.e., before and after the addition of an excess of solid PPh₃. This method was developed and used previously by one of us²¹ for the analysis of reaction mixtures obtained from various alkane oxidations. A Fisons Instruments GC 8000 series gas chromatograph with a capillary column 30 m×0.32 mm×25 µm, DB-WAX (J&W) (helium was the carrier gas; the internal standard was nitromethane) was used. Blank experiments showed that in the absence of precatalyst **1** only very low amount of products was formed.

Acknowledgements

The authors thank the Russian Foundation for Basic Research, grant 12-03-00084-a, and the Fundação para a Ciência e a Tecnologia (FCT), projects PTDC/QUI-QUI/102150/2008 and PEst-OE/QUI/UI0100/2011, for support. G.B.S. and L.S.S. express their gratitude to the FCT for making it possible for them to stay at the Instituto Superior Técnico, TU Lisbon, as invited scientists and to perform a part of the present work.

Appendix. Low probability of the alkane oxygenation by peroxides with the involvement of a classical radical-chain mechanism (ROO+RH=ROOH+R \cdot)

It is known that autoxidation³³ of saturated hydrocarbons in the liquid phase is usually a branched chain process with a so-called 'degenerate' chain branching. This means that branching of each chain happens much later than its termination and is caused by the formation of a rather stable intermediate. This intermediate is nevertheless chemically more active than the initial hydrocarbon and can form free radicals at a greater rate than the rate of the chain initiation process. Autoxidation of compounds containing 'weak' C–H bonds is of great importance for living organisms. Hydroperoxides are the intermediates in liquid phase oxidation. The following classical scheme presents a typical mechanism of liquidphase hydrocarbon oxidation.

Chain initiation:

(A)
$$RH + O_2 \xrightarrow{\kappa_A} R^{\cdot} + HOO^{\cdot}$$

Chain propagation:

(B) $\mathbf{R}^{\cdot} + \mathbf{O}_2 \xrightarrow{k_B} \mathbf{ROO}^{\cdot}$

(C) $\operatorname{ROO}^{\cdot} + \operatorname{RH} \xrightarrow{k_{\mathsf{C}}} \operatorname{ROOH} + \operatorname{R}^{\cdot}$

Chain branching:

- (D) ROOH $\xrightarrow{k_D}$ RO[·] + HO[·] or
- (D') 2ROOH $\xrightarrow{k_{D'}}$ RO[·] + ROO[·] + H₂O

Chain termination:

- $(E) \quad \mathbf{R}^{\cdot} + \mathbf{R}^{\cdot} \rightarrow \mathbf{R} \mathbf{R}$
- (F) $\operatorname{ROO}^{\cdot} + \operatorname{R}^{\cdot} \rightarrow \operatorname{ROOR}^{\cdot}$

(G)
$$\operatorname{ROO}^{\cdot} + \operatorname{ROO}^{\cdot} \xrightarrow{\kappa_G} \operatorname{ROH} + \operatorname{R'COR''} + \operatorname{O}_2$$

Radicals RO• and HO• can take part in the fast following steps:

$$(C'')$$
 HO[·] + RH \rightarrow H₂O + R[·]

$$(C''')$$
 RO[·] + RH \rightarrow ROH + R

Oxidations of alkanes can be initiated by free radicals, X[•], which are capable of abstracting the hydrogen atom from an alkane:

$$(A\prime) \quad X^{\cdot} + RH \rightarrow XH + R^{\cdot}$$

Very reactive hydroxyl and alkoxyl radicals are among potential initiators of alkane oxidations. Radicals initiating the oxidations can be produced by the decomposition of H_2O_2 or *tert*-BuOOH under the action of light or (much more efficiently) of a metal complex catalyst:

$$H_2O_2 \rightarrow HO^{-} + \dots$$

tert-BuOOH \rightarrow tert-BuO⁻ + ...

Molecular oxygen from air could be the oxidant. The catalyzed oxidation of an alkane, RH, with H_2O_2 or *tert*-BuOOH affords in many cases (at least in the beginning of the reaction) the corresponding alkyl hydroperoxide, ROOH. This can testify that chain branching steps (*D*) and (*D'*), which can give the alcohol in the propagation step (*C'''*) should not be involved into the reaction mechanism.

Let us analyse the possibility of a classical radical-chain route with the key stage (C) for the oxygenation of different alkanes having strong and weak C–H bonds. The simplified mechanism of an initiated non-branched radical-chain liquid-phase oxidation of a hydrocarbon, RH, can be described by the following equations.

Chain initiation:

$$\mathbf{R}\mathbf{H} \xrightarrow{W_i} \mathbf{R}^{\cdot} \tag{A1}$$

Chain propagation:

$$R' + O_2 \rightarrow ROO' \tag{A2}$$

$$ROO' + RH \xrightarrow{\kappa_p} ROOH + R'$$
(A3)

Chain termination:

$$\text{ROO}^{\cdot} + \text{ROO}^{\cdot} \xrightarrow{\kappa_t} \text{non-radical products}$$
 (A4)

The rate of alkyl hydroperoxide accumulation, W_{ROOH} , corresponding to the above mechanism can be described by the following equation:

$$W_{\text{ROOH}} = \frac{k_p}{\sqrt{2k_t}} \sqrt{W_i} [\text{RH}]$$
(A5)

Here k_p is the rate constant of the interaction between peroxyl radical and RH [reaction (A3)], and k_t is the rate constant of the chain termination [reaction (A4)]. The chain length of the process ν equals the ratio of the ROOH formation rate and the chain initiation rate:

$$\nu = \frac{W_{\text{ROOH}}}{W_i} \tag{A6}$$

Equations (A5) and (A6) show that the rate W_{ROOH} increases and the chain length ν decreases with increasing W_i . The condition $W_{\text{ROOH}}=W_i$ evaluates the rate of RH oxidation, W^0_{ROOH} , via a radical-chain mechanism with ν =1:

$$W_{\rm ROOH}^{0} = \left(\frac{k_{\rm p}}{\sqrt{2k_{\rm t}}}\right)^2 \times [\rm RH]^2 \tag{A7}$$

At $W_{\text{ROOH}} < W_{\text{ROOH}}^0$ a radical-chain oxidation process is possible $(\nu > 1)$, and at $W_{\text{ROOH}} > W_{\text{ROOH}}^0$ only the radical oxidation of RH with $\nu < 1$ is possible. Thus, it may be stated that comparison of the effective rate of the RH oxidation with the rate calculated using equation (A7) allows us to make a conclusion about either a fundamental possibility or inability to associate the efficient process rate with the chain mechanism of the oxidation. The value of W^{0}_{ROOH} is governed by so-called oxidizability parameter, $k_{p}/\sqrt{2k_{t}}$, and the hydrocarbon concentration. The values of oxidizability parameters are known for certain hydrocarbons, and can be calculated for other ones using values k_p and k_t . For methane and ethane oxidation in the liquid phase the rate constants for chain propagation, $k_{\rm p}$, and chain termination, $k_{\rm f}$, remain unknown. Therefore, any methods of estimation of these parameters, even approximate, are of considerable interest because they allow us to get knowledge about the efficiency of the initiated radical-chain process of liquid-phase oxidation of light hydrocarbons. Calculations have been carried out also for the hydrocarbons, for which direct experimental data are known. Table A1, Section (I) summarizes the rate constants for chain propagation, $\lg k_{\rm p}$, at 30 °C and their dependences on temperature for certain hydrocarbons. To estimate the rate constants k_p we used empirical equation (A8):^{34a}

$$\lg k_p = -B + 0.225 D_{R-H} + \frac{5900 - 98 D_{R-H}}{T}$$
(A8)

Here the parameters are expressed: k_p in M^{-1} s⁻¹, D_{R-H} (i.e., bond energy for the abstracted H atom) in kcal mol⁻¹, and B=-11.5for hydrocarbons containing secondary C–H bonds and -12.5 for hydrocarbons with tertiary C–H bonds. For hydrocarbons having only primary C–H bonds, we accepted the value B=-11.5, that is, equal to the parameter for hydrocarbons containing secondary C–H bonds. Using the same empirical equation (A8) we calculated the temperature dependence of k_p according to the relationships:

$$lgA = -B + 0.225D_{R-H} \quad (M^{-1}s^{-1})$$
 (A9)

$$E = 4.575(5900 - 98D_{R-H}) \times 10^{-3} \quad (kcal \ mol^{-1}) \tag{A10}$$

Here *A* is preexponential factor for the rate constant and *E* is activation energy of the reaction. In our calculations we used either the known from the literature value of bond energy in the hydrocarbon or this parameter was calculated previously according to equation (A8) using the k_p value at the fixed temperature.

The rate constants for chain termination $(\lg 2k_t)$ and corresponding temperature dependences are summarized in Table A1, Section (II). In the cases when the temperature dependences are unknown the values of activation energy were accepted in accordance with the analysis of the literature data^{34b} and for radicals CH₃CH₂OO• and CH₃OO• we used parameters determined for the gas-phase reactions. Section (III) collects also oxidizability parameters at 30 °C,^{34g} the same parameters extrapolated to 30 °C and

Table A1

Parameters for the liquid-phase H atom abstraction from the hydrocarbons, RH, by their peroxyl radicals, ROO[•] (I) and for termination reaction (II), as well as oxidizability parameters (III)

No	Hydrocarbon,	(I) Reaction R	$H+ROO^{\bullet} \rightarrow R^{\bullet}$	+ROOH ^a		(II) Reaction ROO•+ROO• \rightarrow ^a			(III) Hydrocarbon oxidizability ^b	
	RH	lg k_p (30 °C) (M ⁻¹ s ⁻¹)	$lg A (M^{-1} s^{-1})$	E (kcal mol ⁻¹)	D _{R-H} (kcal mol ⁻¹)	$\frac{\lg 2k_t (30 \ ^\circ C)}{(M^{-1} \ s^{-1})}$	$lg 2A_t$ (M ⁻¹ s ⁻¹)	E _t (kcal mol ⁻¹)	$\frac{\lg (k_p / \sqrt{2k_t}) (30 \ ^{\circ}\text{C})}{(L^{\frac{1}{2}} \ \text{mol}^{-\frac{1}{2}} \ \text{s}^{-\frac{1}{2}})}$	E _{eff} (kcal mol ⁻¹)
1	Tetralin	0.97	5.58	6.4		6.82	9.93	4.3	-2.52	3.9
		0.81	4.9 ^c	5.7 ^c						
		0.89 ^d	5.24 ^d	6.05 ^d						
2	Cyclohexene	0.55	5.6	7.0		6.45	10.8	6.0 ^g	-2.56	3.35
	-	0.785	4.9 ^c	5.7 ^c					-2.64^{k}	
		0.67 ^d	5.25 ^d	6.35 ^d					-2.60^{d}	
3	Ethylbenzene	-0.16	5.98	8.5		7.25	9.8	3.5 ^h	-3.78	7.5
		-0.2	4.83	7.0					-3.68 ^k	
		-0.16	7.1 ^c	10.0 ^c					-3.17 ¹	6.8 ¹
		-0.17 ^d	6.0 ^d	8.5 ^d					-3.54^{d}	7.15 ^d
4	Toluene	-0.62	8.1 ^c	12.2 ^c	83	8.48	9.86	2.0	-4.64	10.2
		-0.17	7.2 ^e	10.2 ^e					-5.0 ^k	
		-0.4^{d}	7.65 ^d	11.2 ^d					-4.82^{d}	
5	Cumene	-0.77	6.51	10.1		4.27	8.58	6.0	-2.89	6.25
		-0.745	5.3 ^c	8.4 ^c					-2.82 ^k	
		-0.76^{d}	5.9 ^d	9.2 ^d					-2.83 ¹	6.8 ¹
									-2.85^{d}	6.52 ^d
6	Cyclohexane	-1.23^{f}	9.6 ^f	15.0 ^f	94	6.5	11	6.0 ⁱ	-4.48	12.0
									-5.13 ¹	13.0 ^l
									-4.80^{d}	12.5 ^d
7	Ethane	-1.7	10.5	16.9	98	8.1 ^j	8.4	0.5 ^j	-5.75	16.9
8	Methane	-2.2	11.6	19.2	103	8.7 ^j	8.1	-1^j	-6.55	20

^a From Ref. 34b.

^b The values of oxidizability parameter, $k_p/\sqrt{2k_t}$, and effective activation energy, $E_{eff}=E_p-\frac{1}{2}E_t$, were calculated using the data from Sections (I) and (II).

^c The temperature dependence of k_p has been calculated using k_p value at 30 °C^{34b} and equation (A6).

^d For some hydrocarbons, parameters lg k_p , lg A, E, lg $(k_p/\sqrt{2k_t})$ and E_{eff} were taken (or extrapolated) from different references, and in the last line arithmetical mean values calculated from upper values of the column are given.

^e The parameters were calculated in accord with equation (A8) using values for D_{R-H} taken from Ref. 34c.

^f Calculated according to equation (A8) using lg k_p =-0.275 at 60 °C³

^g Parameter for solution in CH₃OH (Ref. 34d).

^h Calculated based on data from Ref. 34b.

ⁱ Parameter for solution in CH₃COOH (Ref. 34b).

^j Data for the reaction in the gas phase (Ref. 34e,f).

^k From Ref. 34g.

¹ From Ref. 34h.

their temperature dependences according to the literature data,^{34h} as well as these parameters calculated based on the arithmetical mean values given in Sections (I) and (II) of Table A1. Table A1 demonstrates that in the cases of hydrocarbons, for which the experimental parameters are available, the estimated results are in tolerable agreement with the data obtained from direct measurements. Taking this into account, we believe that estimated by us

the 10% transformation of ethane and methane via mechanism (A1)–(A4) the reactions will take 6.5 and 30 days, respectively, which indicates that the highest possible rate of the chain process is extremely low for these hydrocarbons. However, for hydrocarbons with weak C–H bonds, such as tetralin and cyclohexene (allylic methylenes), as well as cumene, corresponding transformations will take less than 1 h and consequently are possible.

Table A2

Highest possible rates of the hydrocarbon radical-chain low-temperature oxidation (chain length $\nu = 1$ and $W^0_{\text{ROOH}} = W_i$) and the minimum possible times $\tau_{0.1}^0$ for the transformation of these hydrocarbons to the extent of $10\%^a$

		Rate W^{0}_{ROOH} (M s ⁻¹)		Time $\tau_{0.1}^{0}$		
No	Hydrocarbon	30 °C	100 °C	30 °C	100 °C	
1	Tetralin	9.1×10 ⁻⁶	1.0×10 ⁻⁴	1.7 h	0.2 h	
2	Cyclohexene	6.3×10^{-6}	5.1×10^{-5}	2.5 h	0.3 h	
3	Ethylbenzene	8.3×10 ⁻⁸	7.3×10^{-6}	7.5 days	2.1 h	
4	Toluene	2.3×10^{-10}	1.0×10^{-7}	7.5 years	6.5 days	
5	Cumene	2.0×10^{-6}	1.2×10^{-4}	7.5 h	0.2 h	
6	Cyclohexane	5.5×10^{-11}	1.0×10^{-7}	32.5 years	6.5 days	
7	Ethane	3.2×10^{-12}	1.0×10^{-7}	550 years	6.5 davs	
8	Methane	7.9×10^{-14}	2.1×10^{-8}	22,000 years	30 days	

^a The parameters have been calculated in assumption of the hydrocarbon concentration of 1.0 M. At $W_{\text{ROOH}} > W_{\text{ROOH}}^0$ the chain length $\nu < 1$, which corresponds to a non-chain process, and at $W_{\text{ROOH}} < W_{\text{ROOH}}^0$ parameter $\nu > 1$ and $\tau_{0.1} > \tau_{0.1}^0$.

values of parameter $k_p/\sqrt{2k_t}$ for ethane and methane can differ from the true values only by a factor of a few times. Using the arithmetical mean values from Table A1 (Section III) we calculated maximum possible rates or the RH oxidation, equal $2W_{\text{ROOH}}^0$, for the process, which occurring in accordance with kinetic scheme (A1)–(A4) with the chain length=1, as well as the minimum time of 10% RH conversion ($\tau_{0,1}$). The parameters W_{ROOH}^0 were calculated according to equation (A7). The conversion time was determined by the integration of equation (A11):

$$-\frac{d[RH]}{dt} = 2\left(\frac{k_{\rm p}}{\sqrt{2k_{\rm t}}}\right)^2 \times [RH]^2 \tag{A11}$$

This expression has been obtained for the kinetic scheme (A1)-(A4) under conditions (A12) and (A13).

$$\nu = \frac{W_{\text{ROOH}}}{W_{\text{i}}} = 1 \tag{A12}$$

$$2\frac{d[\text{ROOH}]}{dt} = -\frac{d[\text{RH}]}{dt}$$
(A13)

Using these equations we can obtain the following expression for the 10% conversion time:

$$\tau_{0.1} = \frac{0.055}{[\text{RH}]_0 \left(\frac{k_p}{\sqrt{2k_t}}\right)^2}$$
(A14)

It can be seen that if ν >1 we have $W_{\text{ROOH}} < W_{\text{ROOH}}^0$ and the $\tau_{0.1}$ value will be higher. Assuming [RH]=1 M we will obtain the expressions for parameters W_{ROOH}^0 and $\tau_{0.1}$. Both equations will contain only the oxidizability parameters. The results of such calculations are summarized in Table A2. It is follows from the data of this table that for a hydrocarbon, such as cyclohexane and especially for much more inert ethane and methane at 30 °C any really obtained rates will sufficiently exceed value of W_{ROOH}^0 , that is, in principle, we have no reason to discuss the possibility of chain process in accordance with scheme (A1)–(A4). Even at 100 °C for

Transition metal ions are often used as catalysts in lowtemperature alkane oxidations. The classical radical-chain mechanism of the alkane oxidation (steps A2, A3 and A4) is the same. Catalysts take part in the initiation stage inducing the initiator decomposition generating free radicals. This case is not different from the initiated alkane oxidation considered above, and here all parameters estimated previously can be used. On the other hand, complex ions of transition metals could effectively interact with alkyl hydroperoxide formed in the oxidation process even at relatively low temperature.^{33b,34b} This interaction results in the peroxide decomposition affording free radicals. In this case we have to add to the scheme (A1)–(A4) the following stages (**M** is an ion of transition metal in oxidized or reduced form):

$$ROOH + \mathbf{M}(ox) \rightarrow ROO^{\bullet} + H^{+} + \mathbf{M}(red)$$
(A15)

$$ROOH + \mathbf{M}(red) \rightarrow RO^{\bullet} + HO^{-} + \mathbf{M}(ox)$$
 (A16)

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$
 (A17)

If in the case of the route (A1)–(A4) the final product of the reaction is alkyl hydroperoxide, ROOH, the pathway (A15)–(A17), which generates branching mechanism, gives rise to the alcohol as a main product. The analysis of the kinetic scheme in the steady-state approximation taking into account expressions (A15)–(A17) gives equation (A18) for the hydrocarbon consumption in the propagation stage.

$$W_{\rm RH} = \frac{3}{2} \left(\frac{k_{\rm p}}{\sqrt{2k_{\rm t}}} \right)^2 \times [\rm RH]^2 \tag{A18}$$

A comparison of expression (A18) and (A7) shows that the rate of the ROOH decomposition with the participation of a catalyst is only 1.5 times higher than the rate of hydrocarbon consumption in the chain termination step. It is important that in the latter case the composition of the products can be dramatically changed. As in some metal-catalyzed oxidations, at least at low (<50 °C) temperatures and at least in the beginning of the reaction cyclohexane and normal alkanes are transformed only into alkyl hydroperoxides, we can disregard a mechanism involving steps (A15)–(A17). Taking this into account, we conclude that, in accordance with data summarized in Table A2, the classical radical-chain mechanism (A1)–(A4) should be neglected for this case. However, the contribution of this pathway might be expected for easily oxidizable hydrocarbons, such as tetralin, cyclohexene, etc. It should be emphasized that our calculations do not exclude the possibility for the oxidation of cyclohexane, methane and other alkanes having strong C–H bonds via a radical *non-chain* mechanism where $W_{\rm RH} < W_i$ ($\nu < 1$). In these processes an active radical or radical-like species (e.g., HO•, O₃SO•⁻, Mn=O) abstracts *one* hydrogen atom from the alkane molecule to afford *one* alkyl radical, which is further transformed into *one* molecule of a product (e.g., of alkyl hydroperoxide). Three possible mechanisms of alkane oxygenation induced by a radical or radical-like species are shown in Scheme A1. Balcells, D.; Sauer, E. L. O.; Raynaud, C.; Brudvig, G. W.; Crabtree, R. H.; Eisenstein, O. *J. Am. Chem. Soc.* **2010**, *132*, 7605–7616; (h) Zeng, X.-M.; Chen, J.-M.; Middleton, K.; Zhdankin, V. V. *Tetrahedron Lett.* **2011**, *52*, 5652–5655.

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Scheme A1. Three mechanisms for oxygenation of alkanes induced by radical or radical-like species X-O*.

Supplementary data

Supplementary data related to this article: S1. Oxygenation of methylcyclohexane. S2. On the possible mechanism of oxygenation of benzene and alkanes by the '1/oxalic acid/Oxone' system. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2012.07.098.

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