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Alkane oxidation by the H_2O_2–$NaVO_3$–H_2SO_4 system in acetonitrile and water

Lidia S. Shul'pina [a], Marina V. Kirillova [b], Armando J.L. Pombeiro [b,*], Georgiy B. Shul'pin [c,*]

[a] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Ulitsa Vavilova, dom 28, Moscow 119991, Russia
[b] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049–001 Lisbon, Portugal
[c] Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ulitsa Kosygina, dom 4, Moscow 119991, Russia

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ABSTRACT

A simple system is described, which oxidizes saturated hydrocarbons either in acetonitrile or (less efficiently) in water. The system consists of 50% aqueous hydrogen peroxide as an oxidant, sodium metavanadate, $NaVO_3$, as a catalyst and sulfuric (or oxalic) acid as a co-catalyst. The reactions were carried out at 20–50 °C. In the oxidation of cyclohexane in acetonitrile, the highest yield (37% based on cyclohexane) and turnover number (TON=1700) were attained after 3 h at 50 °C. The corresponding parameters were 16% and 1090 for *n*-heptane oxidation under the same conditions. The oxidation of higher alkanes, RH, in acetonitrile gives almost exclusively the corresponding alkyl hydroperoxides, ROOH. Light alkanes (*n*-butane, propane, ethane, and methane) have been also oxygenated by the system under consideration. The highest TON (200) was attained for ethane and the highest yield (19%) was obtained in the case of *n*-butane. The selectivity parameters measured for the oxidation of linear and branched alkanes are low, the reaction with *cis*- and *trans*-1,2-dimethylcyclohexanes is not stereoselective. These facts lead us to conclude that the oxidation occurs with the formation of hydroxyl radicals in the crucial step.

1. Introduction

Soluble and solid derivatives of transition metals are known to catalyze oxidations of hydrocarbons with hydrogen peroxide.[1] It should be emphasized that alkanes are very inert organic compounds, and yields and selectivity in their oxidations are usually low. For example, in the commercial oxidation of cyclohexane by air at 160 °C with the participation of Co(II) as a catalyst the reaction is run only to 4% conversion.[1e] The desired compounds constitute only 85% of the products. These compounds are cyclohexanol and cyclohexanone, both of which are also susceptible to further oxidation. Oxidations of alkanes with hydrogen peroxide proceed usually more selectively. However, even in this case yields of products around 30% based on the alkane can be considered as high.[1d,f]

Various vanadium compounds induce transformation of organic compounds [2] including hydrocarbon oxidations with peroxides.[3,4] It has been previously shown that oxovanadium derivatives are good catalysts for hydrogen peroxide oxygenation (i.e., insertion of the oxygen atom into the C–H bond) of saturated hydrocarbons in acetonitrile solution.[5,6] These reactions occur in the presence of pyrazine-2-carboxylic acid[5] or nitric acid[6] as co-catalysts. Methane has been recently oxygenated (TON up to 150) with H_2O_2 in water in the reaction catalyzed by KVO_3 in the presence of perchloric acid in low concentration.[7]

2. Results and discussion

In the present work, we have found that heating a solution of cyclohexane, CyH, in acetonitrile with 50% aqueous hydrogen peroxide in the presence of $NaVO_3$ and H_2SO_4 leads to the efficient oxygenation of the alkane. Examples of the kinetic curves are shown in Figure 1. Since $NaVO_3$ is almost insoluble even in aqueous acetonitrile we used the catalyst as a stock solution prepared by dissolution of the vanadium salt and H_2SO_4 in water (see Experimental). In the experiments shown in graphs B–F (Fig. 1) some amounts of sulfuric acid were added to the reaction solution, whereas in the experiment shown in graph A only H_2SO_4 from the stock solution was used.

Samples of the reaction solutions were analyzed by GC. We used a simple method developed earlier by some of us.[8] The oxygenation of alkanes usually gives rise to the formation of the corresponding alkyl hydroperoxides as the main products. If an excess of solid PPh_3 is added to a sample of the reaction solution, ca. 10 min before 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).

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* Corresponding authors. Fax: +7 495 9397417/6512191 (G.B.S.); fax: +351 21 8464455 (A.J.L.P.).

E-mail addresses: pombeiro@ist.utl.pt (A.J.L. Pombeiro), shulpin@chph.ras.ru, gbsh@mail.ru (G.B. Shul'pin).

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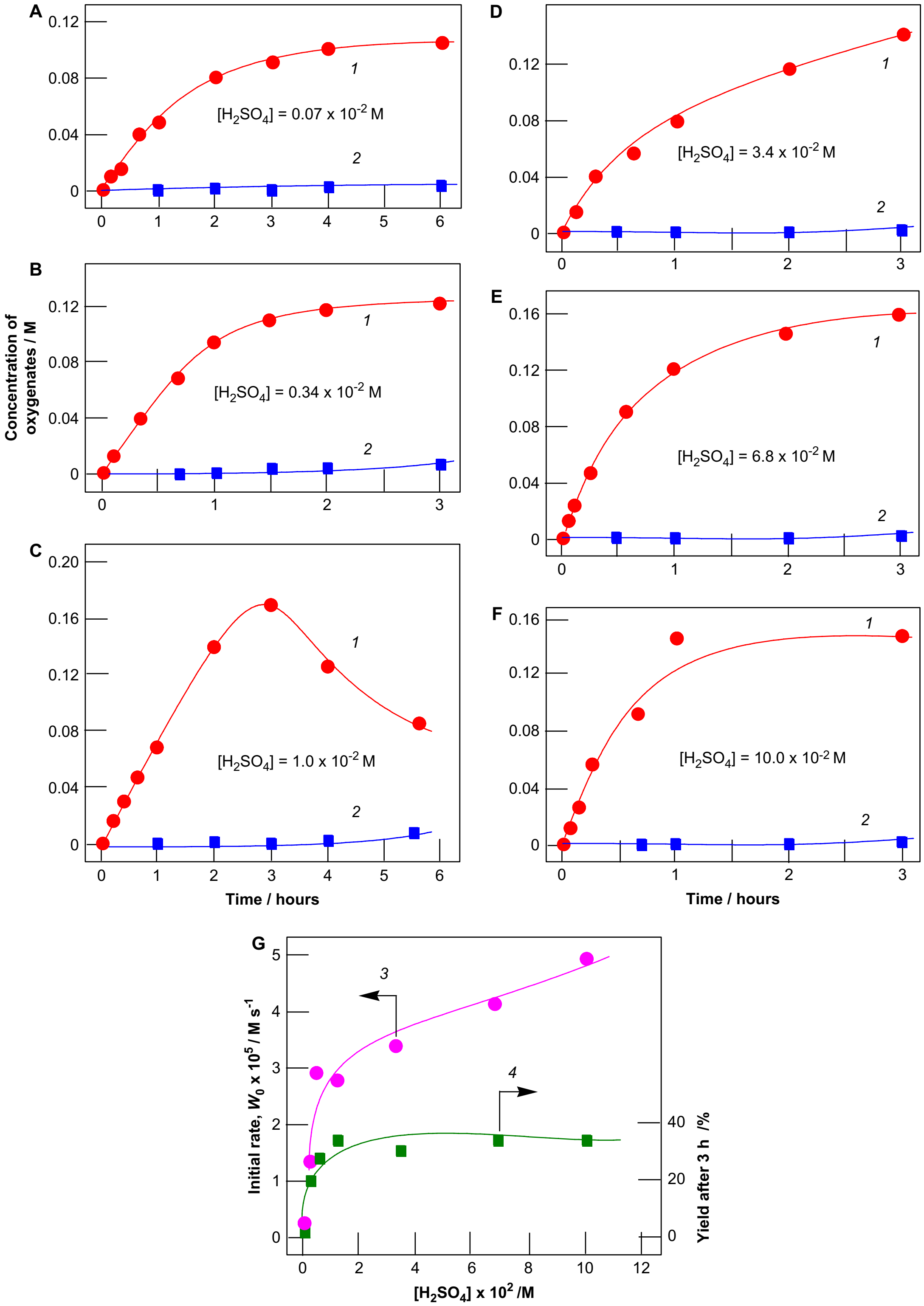

Figure 1. Accumulation of the products (cyclohexyl hydroperoxide, curve 1 as well as the sum cyclohexanol+cyclohexanone, curve 2, graphs A–F) in the oxidation of cyclohexane (0.46 M) with hydrogen peroxide (50% aqueous; 1.47 M) catalyzed by $NaVO_3$ (0.1 mM) in MeCN at 50 °C at various total concentrations of H_2SO_4 (these concentrations are written in graphs A–F). Dependencies of the initial reaction rate W_0 and the product yield after 3 h on the concentration of H_2SO_4 are shown in graph G. Concentrations of cyclohexanone and cyclohexanol were determined twice, before and after reduction of the aliquots with solid PPh_3 (for this method, see Ref. 8).

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. We demonstrate in the present work with this method that the vanadium-catalyzed reaction affords predominantly the cyclohexyl hydroperoxide, CyOOH, whereas cyclohexanone and cyclohexanol are formed in very small amounts (Fig. 1, graphs A–F).

It follows from Figure 1 that the highest yield of the cyclohexyl hydroperoxide (37% based on cyclohexane) and turnover number (1700) can be attained at $[NaVO_3]=0.1$ mM and $[H_2SO_4]=0.01$ M after 3 h at 50 °C (Fig. 1, graph C). Some decomposition of CyOOH occurs after 3 h under these conditions. Graph G demonstrates that there is no substantial increase in yield if the concentration of the sulfuric acid is higher than 0.01 M. However, the initial reaction rate W_0 grows four times when the concentration of the sulfuric acid is changed from 0.07×10^{-2} M to 0.1 M. The data on the *n*-heptane oxidation with the system under consideration are summarized in Table 1. It can be seen that the highest TON=1090 can be attained after 3 h.

The kinetic curves of the CyH oxidations catalyzed by $NaVO_3$ at its higher concentration (1.0 mM) are shown in Figure 2, graphs A, B. The oxidation of cyclohexane carried out at a lower concentration $[NaVO_3]=0.1$ mM is demonstrated in Figure 2, graph. C.

The oxidation in the absence of sulfuric acid proceeds noticeably slower. Thus, under the experimental conditions shown in Figure 2, graph B (viz at $[NaVO_3]=1.0$ mM, $[CyH]_0=0.46$ M, $[H_2O_2]_0=1.47$ M, 50 °C) only 0.015 M of cyclohexyl hydroperoxide was formed after 5 h. The reaction in the presence of sulfuric acid (0.01 M) but in the absence of $NaVO_3$ gave only 0.004 M of CyOOH after 4 h at 50 °C. At the same time, the full catalytic system (which contains both sodium vanadate and sulfuric acid) efficiently oxidizes cyclohexane even at room temperature with the TON attaining 1600 after 48 h (Fig. 3).

Other strong inorganic and carboxylic acids can be used in the combination with sodium vanadate for the efficient alkane oxidation. For example, the cyclohexane oxygenation co-catalyzed by oxalic acid occurs with TON=1200 after 2 h at 50 °C (Fig. 4).

Alkanes can be oxidized by this system in water solution in a biphasic system. Thus, cyclohexane (1.15 mmol) after the reaction with $NaVO_3$ (0.0005 mmol), H_2SO_4 (0.01 mmol), and H_2O_2 (7.3 mmol) gave cyclohexanol (0.45 mmol after reduction with PPh_3) with TON 90. We have also found that the system oxidizes light alkanes both in acetonitrile and water. The results are summarized in Table 2. It can be seen that the oxidation of *n*-butane occurs in 19% yield and the TONs in the oxidation of propane and ethane are ca. 200. The oxidation in water is noticeably less efficient.

The regioselectivity parameters determined for the oxidation of *n*-heptane (Tables 1 and 3, entries 1,2) and *n*-octane (Table 3, entries 1,2) are low, C(1):C(2):C(3):C(4)≈1:(5–10):(5–10):(5–10). These values are close to the parameters determined previously for systems, which oxidize alkanes with participation of hydroxyl radicals (compare with the parameters summarized in entries 3–8 of Table 3). It is clear that the corresponding selectivity parameters for the systems that do not involve active oxygen-centered radicals (entries 9–12) are noticeably higher. The bond-selectivity parameter (1°:2°:3°) in the oxidation of methylcyclohexane by the H_2O_2–$NaVO_3$–H_2SO_4 system, as in the case of linear alkanes, is close to the values of parameters found for the systems oxidizing alkanes with participation of hydroxyl radicals (compare with the parameters summarized in entries 3–8 of Table 3). The oxidation of *cis*- and *trans*-1,2-dimethylcyclohexanes proceeds non-stereoselectively as the trans/cis ratios of isomeric alcohols (after reduction with PPh_3) were ca. 1 (Table 3).

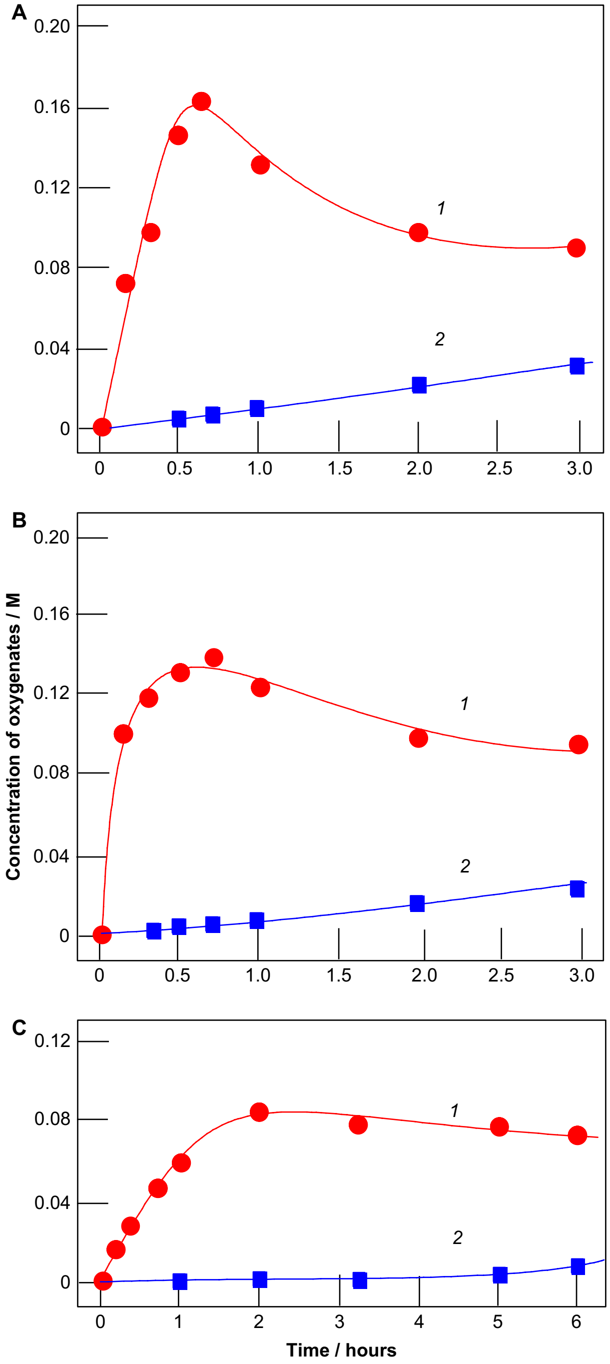

Figure 2. Accumulation of the products (cyclohexyl hydroperoxide, curve 1 as well as the sum cyclohexanol+cyclohexanone, curve 2) in the oxidation of cyclohexane with hydrogen peroxide (50% aqueous; 1.47 M) catalyzed by $NaVO_3$ in MeCN at 50 °C at various initial concentrations of the components. Graph A: $NaVO_3$ (1.0 mM); $[H_2SO_4]_{total}=7\times10^{-3}$ M; cyclohexane (0.46 M). Graph B: $NaVO_3$ (1.0 mM); $[H_2SO_4]_{total}=1\times10^{-2}$ M; cyclohexane (0.46 M). Graph C: $NaVO_3$ (0.1 mM); $[H_2SO_4]_{total}=1\times10^{-2}$ M; cyclohexane (0.23 M). Concentrations of cyclohexanone and cyclohexanol were determined twice, before and after reduction of the aliquots with solid PPh_3 (for this method, see Ref. 8).

Table 1

Oxidation of *n*-heptane with the H_2O_2–$NaVO_3$–H_2SO_4 system[a]

Time (h)	Concentration (mM)							Regioselectivity[b]
	one-2	one-3	one-4	ol-1	ol-2	ol-3	ol-4	
0.25	0.2	0.2	0.0	2.1	8.5	8.8	3.6	1.0:6.1:6.3:5.1
0.50	0.5	0.5	0.0	3.0	16.2	16.6	7.0	1.0:8.1:8.3:7.0
1	1.3	1.3	0.4	5.0	25.0	25.0	11.0	1.0:7.5:7.5:6.6
2	3.0	3.0	2.0	6.0	34	34	15	1.0:8.5:8.5:7.5
3	4.0	5.0	4.0	8.0	36	35	17	1.0:6.8:6.6:6.4
5	6.0	8.0	6.0	4.5	29	29	15	1.0:9.7:9.7:9.9

[a] Reaction conditions: *n*-heptane, 0.7 M; H_2O_2, 1.5 M; $NaVO_3$, 0.1 mM; H_2SO_4, 0.01 M; solvent MeCN; homogeneous solution at 50 °C. Concentrations of the products were measured after reduction with PPh_3. The maximum turnover number (TON, moles of the products per mol of catalyst) 1090 was attained after 3 h. Concentration of heptanal was <0.1 mM.

[b] Relative reactivities of hydrogen atoms at carbons 1, 2, 3, and 4, C(1):C(2):C(3):C(4), of the *n*-heptane chain. The calculated reactivities from the concentrations of alcohols after reduction with PPh_3 parameters were normalized, i.e., calculated taking into account the number of hydrogen atoms at each carbon.

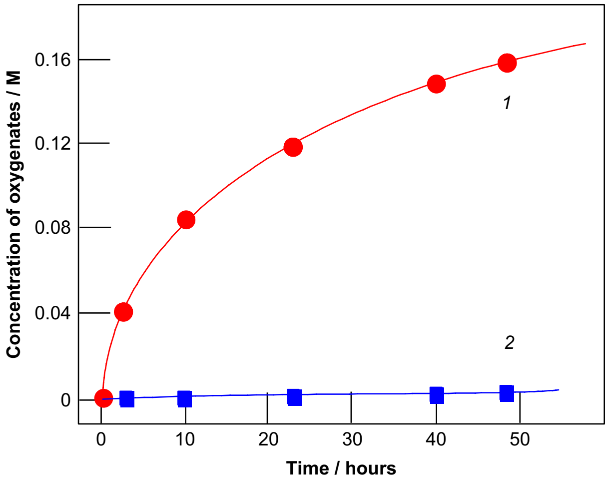

Figure 3. Accumulation of the products (cyclohexyl hydroperoxide, curve 1 as well as the sum cyclohexanol+cyclohexanone, curve 2) in the oxidation of cyclohexane (0.46 M) with hydrogen peroxide (50% aqueous; 1.47 M) catalyzed by $NaVO_3$ (0.1 mM) in MeCN at 20 °C in the presence of H_2SO_4 (0.01 M). Concentrations of cyclohexanone and cyclohexanol were determined twice, before and after reduction of the aliquots with solid PPh_3 (for this method, see Ref. 8).

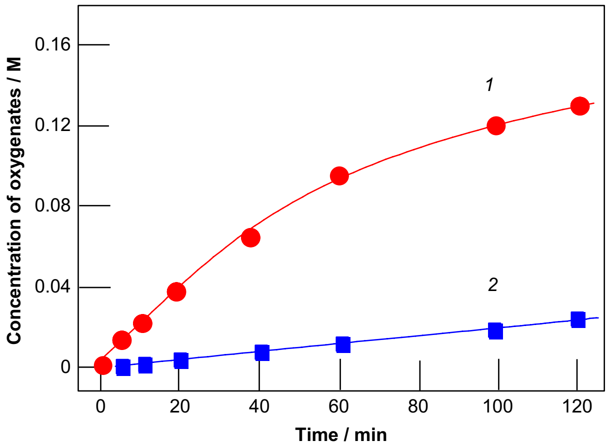

Figure 4. Accumulation of the products (cyclohexyl hydroperoxide, curve 1 as well as the sum cyclohexanol+cyclohexanone, curve 2) in the oxidation of cyclohexane (0.46 M) with hydrogen peroxide (50% aqueous; 1.47 M) catalyzed by $NaVO_3$ (0.1 mM) in MeCN at 50 °C at the presence of oxalic acid (0.02 M). Concentrations of cyclohexanone and cyclohexanol were determined twice, before and after reduction of the aliquots with solid PPh_3 (for this method, see Ref. 8).

On the basis of the selectivity parameters (which are low), we can assume that the alkane oxidation reaction proceeds via the formation of hydroxyl radicals. Vanadate anion under the action of acid is transformed into oligomeric oxovanadates.[14] The yellow color of the initial stock solution indicates the formation of polyvanadates when sulfuric acid is added to the suspension of $NaVO_3$ in water. Under the action of the first H_2O_2 molecule, vanadium(V) ion in the oligomer is reduced to vanadium(IV) (Eq. 1), as it has been proposed previously for another system.[5] The second hydrogen peroxide molecule reacts with the V(IV) derivative to generate the hydroxyl radical (Eq. 2). The hydroxyl radical attacks the alkane molecule, RH (Eq. 3), and the formed alkyl radical reacts rapidly with the oxygen molecule (Eq. 4). The alkyl peroxy radical, ROO$^•$, is further transformed into the alkyl hydroperoxide, which is the primary and main product of our reaction. The perhydroxyl radical, HOO$^•$, is known to react with the V(IV) and V(V) complexes.[15]

$$\mathrm{V(V)} + \mathrm{H_2O_2} \rightarrow \mathrm{V(IV)} + \mathrm{HOO^•} + \mathrm{H^+} \tag{1}$$

$$\mathrm{V(IV)} + \mathrm{H_2O_2} \rightarrow \mathrm{V(V)} + \mathrm{HO^•} + \mathrm{HO^-} \tag{2}$$

$$\mathrm{HO^•} + \mathrm{RH} \rightarrow \mathrm{H_2O} + \mathrm{R^•} \tag{3}$$

$$\mathrm{R^•} + \mathrm{O_2} \rightarrow \mathrm{ROO^•} \tag{4}$$

In the presence of CCl_4 or CBr_4 the rate of cyclohexane oxygenation is noticeably lower, and RCl or RBr is formed, respectively. This testifies that alkyl radicals R$^•$ take part in the oxidation process as it was shown for other systems operating via the formation of hydroxyl radicals.[5a]

3. Conclusions

The system described in the present work can be employed for the hydroperoxidation of alkanes by a cheap green reagent (hydrogen peroxide) at low temperature and in acetonitrile or water (less efficiently), which is believed to occur via formation of the hydroxyl radical. The hydroxyl radical attacks the alkane molecule, and the formed alkyl radical reacts rapidly with the oxygen molecule to generate the corresponding alkyl peroxy radical, which is further transformed into the alkyl hydroperoxide.

4. Experimental section

The catalyst and co-catalyst were used in the form of a stock solution prepared by the following procedure. Concentrated H_2SO_4 (0.1 mL; 1.7 mmol) was slowly added to a mixture of

Table 2

Oxidation of light alkanes with the H_2O_2–$NaVO_3$–H_2SO_4 system[a]

Alkane, (pressure, bar; mmol)	Solvent	$NaVO_3$, (mmol)	Products, (mmol)	TON	Yield, %[b]
n-Butane (1; 1.4)	MeCN	0.005	MeCOEt (0.125), EtCH(OH)Me (0.105), $EtCH_2CHO$ (0.03)	52	19[c]
Propane (8; 11)	MeCN	0.005	Acetone (0.35), isopropanol (0.4), *n*-propanol (0.19), propanal (0.026), propionic acid (0.04)	200	14
Propane (8; 11)	H_2O[d]	0.005	Acetone (0.035), isopropanol (0.006), propanal (0.009), propionic acid (0.009)	12	1
Propane (8; 11)	H_2O[e]	0.005	Acetone (0.017), isopropanol (0.006)	5	0.3
Ethane (30; 41)	MeCN	0.005	Ethanol (0.48), acetaldehyde (0.30), acetic acid (0.16)	190	13
Methane (35; 48)	MeCN	0.0005	Methanol (0.03)	60	0.3
Methane (35; 48)	MeCN	0.005	Methanol (0.025)	5	0.3

[a] Reaction conditions: H_2O_2, 7.3 mmol; H_2SO_4, 0.01 mmol; 4 h at 50 °C. Total volume of the reaction solution was 5 mL. Volume of the autoclave was 39 mL. Concentrations of the products were measured after reduction with PPh_3 (for this method, see Ref. 8).

[b] Based on H_2O_2.

[c] Based on *n*-butane.

[d] Water was added to the total volume of the reaction solution 5 mL.

[e] Total volume of the reaction solution was 0.6 mL.

Table 3
Selectivity parameters in oxidation of linear and branched alkanes by certain oxidizing systems[a]

Entry	System	C(1):C(2):C(3):C(4)		1°:2°:3°	trans/cis	
		n-Heptane	*n*-Octane	MCH	*cis*-DMCH	*trans*-DMCH
1	$NaVO_3–H_2SO_4–H_2O_2$ (MeCN, 50 °C)	1:6.9:6.6:6.5	1.0:10.1:10.7:8.4	1:7:26	0.86	0.90
2	$NaVO_3–H_2SO_4–H_2O_2$ (H_2O, 50 °C)	1:8:7:8	1:7:6:5	1:7:18	1.0	1.0
3	*n*-Bu_4NVO_3–PCA–H_2O_2 (MeCN, 40 °C)[b]	1:5.7:7.2:5.0	1:6.7:7.5:5.3	1:9:37	0.75	0.8
4	hν–H_2O_2 (MeCN, 20 °C)	1:7:6:7	1:10.2:6.8:6.3	1:2:6	0.9	1.0
5	$FeSO_4–H_2O_2$ (MeCN, 20 °C)	1:5:5:4.5			1.3	1.2
6	$Ni(ClO_4)_4$–TMTACN–H_2O_2(MeCN, 70 °C)[c]	1:6.3:7.2:6.1		1:7:15		
7	**1**–H_2O_2 (MeCN, 60 °C)[d]	1:5.5:5.0:4.6		1:4:10	0.9	
8	$H_2O_2–Al(NO_3)_3$ (MeCN, 70 °C)[e]	1:5.3:5.4:4.9	1:5.6:5.6:5.0	1:6:23	0.8	0.8
9	*m*-CPBA (MeCN, 25 °C)	1:36:36.5[f]		1:89:750	0.65	
10	H_2O_2 in CF_3COOH	1:364:363[f]			RC[g]	RC[g]
11	$NaAuCl_4–H_2O_2$ (MeCN, 75 °C)[h]	1:35:25:23		1:116:255		
12	**2**–$MeCO_2H–H_2O_2$ (MeCN, 25 °C)[i]	1:46:35:34	1:29:25:24	1:26:200	0.34	4.1

[a] Parameters C(1):C(2):C(3):C(4) are relative reactivities of hydrogen atoms at carbons 1, 2, 3, and 4 of the *n*-heptane or *n*-octane chain. Parameters 1°:2°:3° are relative normalized reactivities of the hydrogen atoms at primary, secondary, and tertiary carbons of branched alkanes. The calculated reactivities from the concentrations of alcohols after reduction with PPh_3 parameters were normalized, i.e., calculated taking into account the number of hydrogen atoms at each carbon. Parameter trans/cis is determined as the ratio of the formed tertiary alcohol isomers with mutual trans and cis orientation of the methyl groups. Abbreviations: MCH is methylcyclohexane; *cis*-DMCH and *trans*-DMCH are isomers of 1,2-dimethylcyclohexane.

[b] For this system, which is believed to oxidize substrates via formation of hydroxyl radicals, see Ref. 5.

[c] TMTACN is 1,4,7-trimethyl-1,4,7-triazacyclononane. For this system, see Ref. 9.

[d] **1** is complex (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium. For this system, see Ref. 10.

[e] For this system, see Ref. 11.

[f] *n*-Hexane was used instead of *n*-heptane.

[g] RC, retention of configuration.

[h] For this system, see Ref. 12.

[i] **2** is complex $[Mn_2L_2(\mu\text{-}O)_2]^{2+}$ where L is 1,4,7-trimethyl-1,4,7-triazacyclononane. For these systems, see Ref. 13.

$NaVO_3·4H_2O$ (48.5 mg; 0.25 mmol) and H_2O (4.9 mL) at room temperature. The formed mixture was stirred during approx. 10 min until a yellow homogeneous solution was formed. The stock solution containing oxalic acid was prepared analogously. Aliquots of these solutions were added to the reaction mixtures in alkane oxidations.

The reactions of alkanes were typically carried out in air in thermostated (50 °C) Pyrex cylindrical vessels with vigorous stirring (*CAUTION*: the combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive!). The reactions were stopped by cooling, and analyzed twice, i.e., before and after the addition of an excess of solid PPh_3. This method was developed and used previously by some of us[8] 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. The reactions in water were analyzed analogously after addition of acetonitrile to the sample of the final reaction solution.

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