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Oxidation of Saturated Hydrocarbons to Alkyl Hydroperoxides by a 'H_2O_2/Titanosilicalite-1/NaOH/MeCN' System

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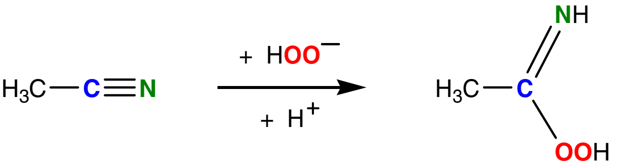
Abstract Hydrogen peroxide oxidizes alkanes at room temperature to produce the corresponding alkyl hydroperoxides in the presence of titanosilicalite-1, NaOH and acetonitrile. The reaction proceeds with low regio- and bond-selectivity and its mechanism apparently involves the formation of hydroxyl radicals.

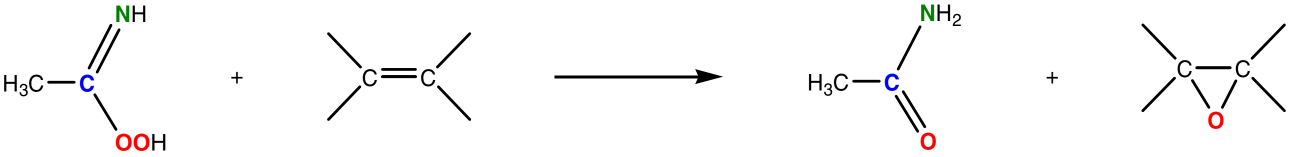
Keywords Alkanes · Alkyl hydroperoxides · Hydrogen peroxide · Titanium catalysts · Nano structures · Oxidation

1 Introduction

Hydrogen peroxide is widely used for oxygenation of hydrocarbons [1], particularly olefins [2] and alkanes [3]. In 1961, Payne described the epoxidation of olefins with H_2O_2 in the presence of nitriles and bases [4]. This reaction was further studied by other authors [5a–f]. Carbodiimide has been used instead of a nitrile [5]. It has been more recently shown that olefin epoxidation with hydrogen peroxide in the presence of nitriles can be catalyzed by anionic clays hydrotalcites (homogeneous basic mixed hydroxides) [2, 6]. It is assumed that hydrogen peroxide is transformed under the action of a base into a perhydroxyl anion, HOO^-, which then attacks the nitrile to generate a peroxycarboximidic acid:



The latter reacts with the olefin to afford the corresponding epoxide and an amide:



In the absence of an olefin hydrogen peroxide decomposes in the acetonitrile solution under the action of a base to produce molecular oxygen in a singlet form (Radziszewski reaction) [7]:

$$CH_3 - CN + H_2O_2 \rightarrow CH_3 - C(=O)NH_2 + 0.5\,{}^1O_2$$

Micro- and mesoporous materials catalyze oxidations of hydrocarbons with H_2O_2 [8]. For example, microporous titanosilicalite TS-1 is known as a catalyst for H_2O_2 oxidation of various organic compounds, mainly for olefin epoxidation (see recent publications [9]). Due to the relatively narrow

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pores, TS-1 catalyzes efficiently the H_2O_2 oxidation of small organic molecules whereas the bulky oxidant, *tert*-butyl hydroperoxide, is inactive in TS-1-catalyzed reactions. However, certain species supported on TS-1 can oxidize bulky molecules [10]. Only a few papers have been devoted to the oxidation of saturated hydrocarbons [11].

We have recently studied [12] the catalyzed by titanosilicalite TS-1 oxidation of lower and higher linear alkanes with aqueous H_2O_2 in the absence of any solvent. Continuing this work we decided to explore the effect of various additives on the oxidation of higher alkanes. It turned surprisingly out that simultaneous addition of acetonitrile and NaOH to the reaction mixture dramatically changes cardinal features of the oxidation and consequently switches the mechanism of the process.

2 Experimental

A titanium-containing zeolite TS-1 was prepared by hydrothermal crystallisation of a silicon–titanium gel containing a tetrapropylammonium salt as described previously [13]. The Si/Ti ratio of 20 was obtained by spectroscopic methods and the specific surface area, measured by gas adsorption (BET), was approximately 373 m^2 g^{-1}. A 50% aqueous solution of hydrogen peroxide ("Fluka") was used for the reactions.

The reactions of alkanes were carried out in air in thermostated (25 °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, acetonitrile containing a small amount of nitromethane (an internal standard for the GC analysis) was then added and the solid TS-1 was filtered off. Other details are given in Figure captions. Each sample was analyzed by GC (a PerkinElmer Clarus 500 chromatograph with capillary column 30 m × 0.22 mm × 25 μm, SGE BP20; helium was the carrier gas) twice, i.e. before and after the addition of an excess of solid PPh_3. This method was used previously by some of us [3, 14] for the analysis of reaction mixtures obtained from various alkane oxidations. Our method was employed more recently by other chemists for the analysis of reaction products and detection of alkyl hydroperoxides in various oxidations of C–H compounds by molecular oxygen, hydrogen peroxide and other peroxides (see, for example, [15]).

3 Results and Discussion

Previously we demonstrated that *n*-hexane, *n*-heptane and *n*-octane can be oxidized by H_2O_2 in the presence of TS-1 at a relatively low temperature (50 °C) in the absence of any organic additives to give a mixture of isomeric alcohols and ketones [12]. We analyzed the reaction solutions by a method developed and used in previous works by some of us [3, 14]. This method is based on comparison of the chromatograms of the reaction solution made before and after the treatment of the sample with triphenylphosphine. Usually alkyl hydroperoxides are decomposed in the chromatograph to produce the corresponding alcohol and ketone. If an excess of solid triphenylphosphine is added to the reaction solution ca. 10 min before 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 the three products (i.e., alcohol, ketone and alkyl hydroperoxide) present in the reaction solution [3, 14]. Application of the method described in Refs. [3, 14] to the oxidation of alkanes, RH, by the '$TS\text{-}1/H_2O_2$' system has demonstrated that only very small amounts of the corresponding alkyl hydroperoxides, ROOH, were formed. In oxidations of linear alkanes by the '$TS\text{-}1/H_2O_2$' system, methyl groups are much more inert in comparison with methylene groups and the regioselectivity parameter C(1):C(2):C(3):C(4) was high (Table 1, entry 1). This observation clearly testifies that the alkane oxidation does not involve free hydroxyl radicals. The reaction occurs possibly with participation of titanium peroxy or oxo species. It is important to note that branched alkanes such as 2- and 3-methylhexane or methyl- and dimethylhexanes cannot be oxidized by this system (Table 1, entry 1). One more feature of the reaction is its unique regio-selectivity. Thus, in the case of *n*-heptane, the CH_2 groups in position 3 exhibit a reactivity 2.5 times higher than other methylenes. It can be assumed that this unusual regioselectivity is due to the narrow hydrophobic cavities of TS-1 in which the oxygenation of alkanes proceeds, and to the U-shape conformation adopted by the *n*-alkane adsorbed on the silicalite [12].

In the present work, we studied the alkane oxidation with hydrogen peroxide in acetonitrile in the presence of a small amount of NaOH. It turned out that the oxidation by the 'H_2O_2/titanosilicalite-1/NaOH/MeCN' system exhibits sufficiently different peculiarities in comparison with the oxidation by H_2O_2 in the absence of a solvent described earlier [12]. The reactions were carried out at room temperature and hydrogen peroxide was added to the reaction mixture portion by portion during 0.5 h in order to avoid non-productive decomposition of H_2O_2 to water and molecular oxygen. The analysis of the reaction mixture by

Table 1 Selectivity parameters in oxidation of linear, branched and cyclic alkanes by the 'H_2O_2/TS-1/NaOH/MeCN' system as well as (for comparison) by certain other oxidizing systems

Entry	System	C(1):C(2):C(3):C(4)[a]			1°:2°:3°[b]				*Trans*/*cis*[c]	
		n-Hexane	*n*-Heptane	*n*-Octane	2,2,4-TMP	MCH	2-MH	3-MH	*cis*-DMCH	*trans*-DMCH
1	H_2O_2/TS-1[d]	1:80:156	1:80:193:100	1:80:62:59	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.
2	H_2O_2/TS-1/NaOH/MeCN[e]	1:6.3:5.9	1:7.7:8.4:7.6	1:6.5:6.6:6.2	1:1.2:2.6	1:5.7:21	1:4:25	1:7:20	0.86	0.94
3	hν–H_2O_2 (MeCN, 20 °C)	1:10:7	1:7:6:7	1:10.2:6.8:6.3	1:2:6	1:2:6	1:6:20	1:4:12	0.9	1.0
4	$FeSO_4$–H_2O_2 (MeCN, 20 °C)		1:5:5:4.5		1:3:6				1.3	1.2
5	*n*-Bu_4NVO_3–PCA–H_2O_2 (MeCN, 40 °C)[f]	1:6.9:7.0	1:5.7:7.2:5.0	1:6.7:7.5:5.3	1:1.5:10		1:9:37	1:14:64	0.75	0.8
6	$Ni(ClO_4)_4$–TMTACN–H_2O_2 (MeCN, 70 °C)[g]		1:6.3:7.2:6.1		1:2.3:4.5	1:7:15		1:5.3:55		
7	**1**-H_2O_2 (MeCN, 60 °C)[h]	1:6.2:7.1	1:5.5:5.0:4.6		1:5:8.5	1:4:10		1:6:19	0.9	
8	MCPBA (MeCN, 25 °C)	1:36:36.5				1:20:520		1:89:750	0.65	
9	H_2O_2 in CF_3COOH[i]	1:364:363			1:52:0				RC	RC
10	$NaAuCl_4$–H_2O_2 (MeCN, 75 °C)[j]		1:35:25:23		1:10:240	1:116:255		1:13:100		
11	**2**-$MeCO_2H$–H_2O_2 (MeCN, 25 °C)[k]		1:46:35:34	1:29:25:24	1:5:55	1:26:200	1:19:204	1:22:200	0.34	4.1
12	**2**-oxalic acid–TBHP (MeCN, 50 °C)[k]		1:14:13:12	1:17:12:15	1:0.4:32	1:0.3:0.6			0.2	7.3
13	**3**-oxalic acid–H_2O_2 (MeCN, 25 °C)[l]	1:71:78	1:91:99:68	1:94:99:51	1:5.3:17				0.31	13
14	**3**-oxalic acid–TBHP (MeCN, 50 °C)[l]		1:76:32:23	1:25:18:12						

[a] Parameters C(1):C(2):C(3):C(4) are relative 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

[b] Parameters 1°:2°:3° are relative normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of branched alkanes. Abbreviations: 2,2,4-TMP, 2,2,4-trimethylpentane (isooctane); MCH, methylcyclohexane; 2- and 3-MH, 2- and 3-methylhexanes

[c] Parameter *trans*/*cis* is the ratio of *trans*- and *cis*-isomers of *tert*-alcohols formed in the oxidation of dimethylcyclohexanes (*cis*-DMCH and *trans*-DMCH)

[d] Reaction conditions: TS-1, 5 mg; *n*-alkane, 0.05 mL; H_2O_2, 0.5 mL, 50 °C; 0.5 h. For this system, see Ref. [12]. No products were formed, n.p

[e] Reaction conditions: TS-1, 5 mg; NaOH (used as 12.5 M solution in water), 0.19 mmol; CH_3CN, 3 mL; 25 °C; H_2O_2 (50% aqueous), total 8.2 mmol was added to the reaction mixture portion by portion during 0.5 h. All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols

[f] For this system, which is believed to oxidize substrates via formation of hydroxyl radicals, see Ref. [16]

[g] TMTACN is 1,4,7-trimethyl-1,4,7-triazacyclononane. For this system, see Ref. [17]

[h] **1** is complex (2,3-η-1,4-diphenylbut-2-en-1,4-dione) undecacarbonyl triangulotriosmium. For this system, see Ref. [18]

[i] For this system, see Ref. [19]. RC, retention of configuration

[j] For this system, see Ref. [20]

[k] **2** is complex $[Mn_2L_2(\mu\text{-}O)_2]^{2+}$ where L is 1,4,7-trimethyl-1,4,7-triazacyclononane. For this system, see Ref. [21]

[l] **3** is complex $[Mn_2(R\text{-}L^{Me2R})_2(\mu\text{-}O)_2]^{3+}$ where R-L^{Me2R} is (*R*)-1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane. For this system, see Ref. [22]

GC before and after reduction with triphenylphosphine [3, 14] showed that in the presence of a small amount of NaOH only alkyl hydroperoxides are formed in relatively high concentrations. No alkane oxidation has been noticed if any component of the system was absent. The hydroperoxidation of cyclohexane has been studied in more detail. Dependences of the amounts of cyclohexyl hydroperoxide on the initial amounts of a substrate (Fig. 1) and the oxidant (Fig. 2) showed that at relatively large amounts of cyclohexane (>2 mmol) or hydrogen peroxide (>8 mmol) the product yield does not depend more on the initial amount of the reactants. The dependence of the yield on the catalyst amount under our conditions passes through the maximum at TS-1 ≈ 5 mg (Fig. 3). The yield of cyclohexyl hydroperoxide attains 3% based on initial cyclohexane. Some not substantial decomposition of hydrogen peroxide to afford molecular oxygen and water occurs in the course of the alkane oxygenation.

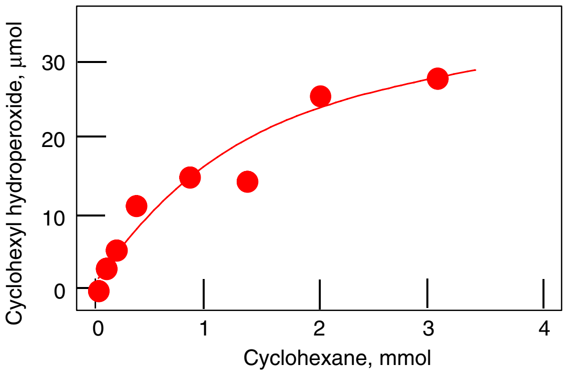

Fig. 1 Dependence of the yield of cyclohexyl hydroperoxide on the initial amount of cyclohexane. Conditions: TS-1, 5 mg; NaOH (used as 12.5 M solution in water), 0.19 mmol; CH_3CN, 3 mL; 25 °C; H_2O_2 (50% aqueous), total 8.2 mmol was added to the reaction mixture portion by portion during 0.5 h

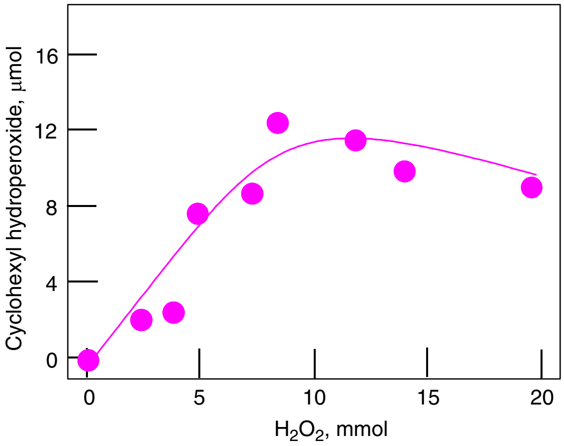

Fig. 2 Dependence of the yield of oxygenates (at $H_2O_2 > 10$ mmol substantial amounts of cyclohexanol and cyclohexanone are formed in addition to cyclohexyl hydroperoxide) on the amount of H_2O_2. Conditions: TS-1, 5 mg; cyclohexane, 9.3 mmol; NaOH (used as 12.5 M solution in water), 0.19 mmol; CH_3CN, 3 mL; 25 °C; H_2O_2 was added to the reaction mixture portion by portion during 0.5 h

Interestingly, a very sharp maximum has been found for the yield dependence on the amount of added NaOH (Fig. 4). It can be seen that the intensive hydroperoxidation of cyclohexane occurs only if the amount 0.1 mmol $< \text{NaOH} < 0.5$ mmol is used [23]. Acetonitrile is an obligatory component of the oxidizing system. No cyclohexyl hydroperoxide has been found when acetonitrile was used in an amount <2 mL (Fig. 5). When acetonitrile was replaced by acetone, cyclohexyl hydroperoxide was not detected. The efficiency of the reaction became much lower at 0 °C instead of typical 25 °C. Increasing the temperature from 25 to 50 °C only insufficiently changes the product yield, however at 40 and 50 °C noticeable amounts of cyclohexanone and cyclohexanol were found by the method using triphenylphosphine which was developed by some of us [3, 14] (Fig. 6).

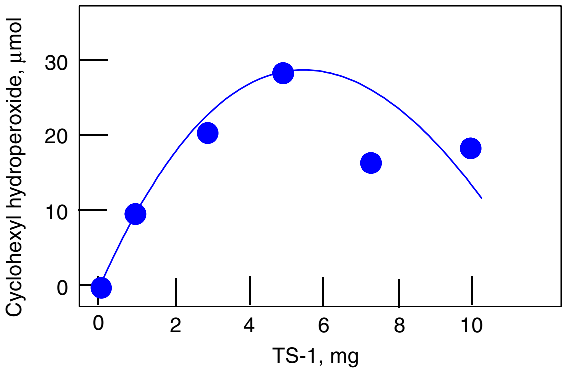

Fig. 3 Dependence of the yield of cyclohexyl hydroperoxide on the amount of TS-1. Conditions: cyclohexane, 3.24 mmol; NaOH (used as 12.5 M solution in water), 0.2 mmol; 25 °C; H_2O_2 (50% aqueous), total 8.2 mmol was added to the reaction mixture portion by portion during 0.5 h; CH_3CN, 3 mL

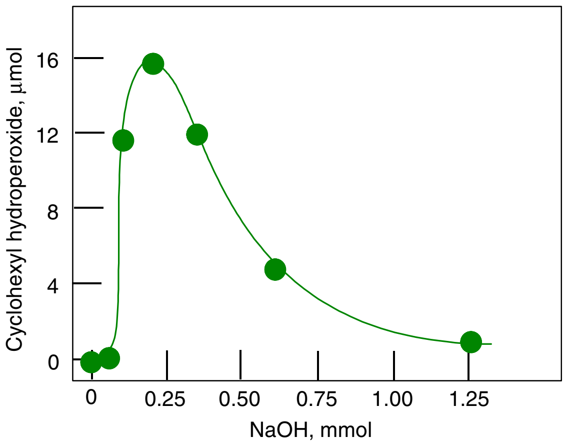

Fig. 4 Dependence of the yield of cyclohexyl hydroperoxide on the amount of NaOH. Conditions: TS-1, 5 mg; cyclohexane, 9.3 mmol; CH_3CN, 3 mL; 25 °C; H_2O_2 (50% aqueous), total 8.2 mmol was added to the reaction mixture portion by portion during 0.5 h

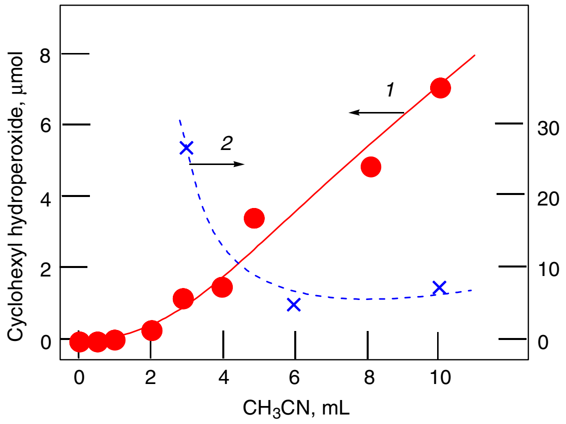

Fig. 5 Dependence of the yield of cyclohexyl hydroperoxide on the volume of acetonitrile. Conditions: TS-1, 5 mg; cyclohexane, 4.6 mmol; NaOH (used as 12.5 M solution in water), 1.25 mmol (curve 1) or 0.2 mmol (curve 2); 25 °C; H_2O_2 (50% aqueous), total 8.2 mmol was added to the reaction mixture portion by portion during 0.5 h

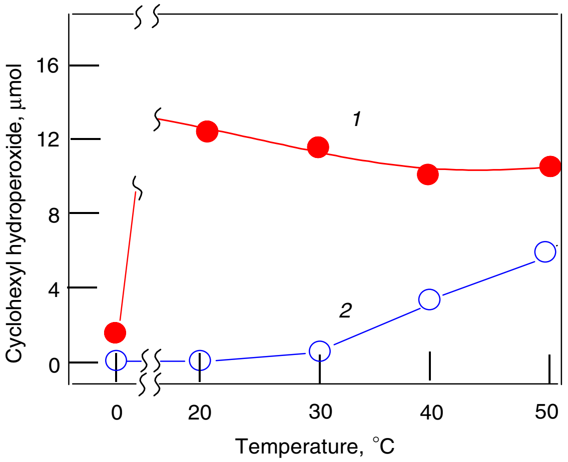

Fig. 6 Dependence of the yield of cyclohexyl hydroperoxide (curve 1) and the sum of cyclohexanol and cyclohexanone (curve 2) on temperature. Conditions: TS-1, 5 mg; cyclohexane, 4.6 mmol; NaOH (used as 12.5 M solution in water), 1.25 mmol; H_2O_2 (50% aqueous), total 8.2 mmol was added to the reaction mixture portion by portion during 0.5 h; CH_3CN, 3 mL

A question arises if the alkane oxidation proceeds on the surface of the heterogeneous catalyst or titanium ions go out to the solution and then homogeneously catalyze the oxygenation. To clarify this point we carried out the following experiment. A mixture of TS-1 (5 mg), NaOH (0.2 mmol), H_2O_2 (0.5 mL) and MeCN (3 mL) was vigorously stirred at 25 °C during 30 min. Solid TS-1 was filtered off and cyclohexane (0.046 mmol) was added to the homogeneous reaction solution. After stirring during additional 60 min the solution was analyzed by GC before and after its reduction with PPh_3. Even traces of the oxygenates have not been detected. In order to eliminate the possibility that this was due to hydrogen peroxide decomposition before the separation of the solid catalyst, promoted by soluble active titanium-containing oxidizing species, we added additional amounts of NaOH and (portion by portion) of H_2O_2. Again, no traces of the oxygenates have been detected after stirring during 30 min. This result testifies that the oxygenation proceeds with the participation of the solid catalyst surface.

Unlike in the oxidation by simple "TS-1/H_2O_2' system, in the presence of NaOH and MeCN, methyl groups of linear alkanes are also intensively oxidized, and parameters of regio- and bond-selectivity are much lower (Table 1, compare entries 1 and 2). For example, for the oxidation of *n*-octane and 3-methylhexane we measured C(1):C(2):C(3):C(4) = 1:6.5:6.6:6.2 and 1°:2°:3° = 1:7:20, respectively (Table 1, entry 2). Naturally, the 'H_2O_2/TS-1/NaOH/MeCN' system oxidizes also branched alkanes. The reaction proceeds non-stereoselectively: for the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane the ratios of isomeric alcohols *trans*/*cis* (after the reduction with PPh_3) were 0.86 and 0.94, respectively. It can be seen from data summarized in Table 1 that selectivity parameters for the 'H_2O_2/TS-1/NaOH/MeCN' system are close to the corresponding values determined previously (see, for example, Refs. 16–18) for the systems that are believed to operate via the formation of hydroxyl radical (entries 3–7) or similar very reactive species. At the same time, these parameters (entry 2) show much less selectivity than that for the oxidations by systems which do not generate hydroxyl or other very active radicals (entries 8–14).

All the data discussed above testify that the formation of the alkyl hydroperoxides proceeds via generation of hydroxyl radicals or similar species such as acyloxy radicals. Possibly, the interaction between H_2O_2, HO^- and then MeCN gives rise to the formation of peroxycarboximidic acid. The latter in the presence of an olefin (and in some cases also of hydrotalcites as catalysts [2, 6]) affords the corresponding epoxide [4, 5]. However, in our system, peroxycarboximidic acid under the action of the TS-1 surfaces decomposes to generate hydroxyl radicals which further attack the alkane. The alkyl radical formed in this process adds rapidly a molecule of oxygen and is transformed finally into the alkyl hydroperoxide. At elevated temperature this alkyl hydroperoxide partially decomposes to give some amounts of the corresponding ketone and alcohol.

As bulky alkanes, such as 2- and 3-methylhexanes, isooctane, 1,2-dimethylcyclohexanes can be easily oxygenated by our system we may assume that the oxidation proceeds not in narrow channels of the TS-1 solid but on its surface. Aliphatic alcohols are usually much more reactive than alkanes. However, they are oxidized by this system with an efficiency comparable to that found in oxygenation of hydrocarbons. Indeed, the oxidation of cyclohexanol (2 mmol) with H_2O_2 (8.2 mmol) in the presence of TS-1 (5 mg) and NaOH (0.19 mmol) in 3 mL MeCN gave 28 μmol cyclohexanone after 0.5 h at 25 °C. This is possibly due to the high hydrophobicity of TS-1.

4 Conclusion

We have discovered here a new system, 'H_2O_2/TS-1/NaOH/MeCN', which oxidizes alkanes at 25 °C. This process relates to the catalyzed version of *olefin epoxidizing* Payne reaction. However, in contrast to the Payne reaction, our system transforms *alkanes* to the corresponding alkyl hydroperoxides.

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